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Selected Processes

IT Enviroscience
Knoxville, TN

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EPA is developing new source performance standards under Section 111 of the Clean Air Act and national emission standards for hazardous air pollutants under Section 112 for volatile organic compound emissions (VOC) from organic chemical manufacturing facilities. In support of this effort, data were gathered on chemical processing routes, VOC emissions, control techniques, control costs, and environmental impacts resulting from control. These data have been analyzed and assimilated into the ten volumes comprising this report.

This volume presents in-depth studies of several major organic chemical products.

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Volume 9: Selected Processes

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1980

02

REPORT 1

FORMALDEHYDE

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Prepared for
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CONTENTS OF REPORT 1

Page

I. ABBREVIATIONS AND CONVERSION FACTORS I-1

II. INDUSTRY DESCRIPTION II-1
- A. Reason for Selection II-1
- B. Formaldehyde Usage and Growth II-1
- C. Domestic Producers II-3
- D. References II-7

III. PROCESS DESCRIPTION III-1
- A. Introduction III-1
- B. Metallic-Silver-Catalyst Process III-2
- C. Metal-Oxide-Catalyst Process III-5
- D. Other Processes III-7
- E. References III-9

IV. EMISSIONS IV-1
- A. Formaldehyde from Methanol Process Using a Metallic Silver Catalyst IV-1
- B. Formaldehyde from Methanol Process Using a Metal Oxide Catalyst IV-6
- C. References IV-12

V. APPLICABLE CONTROL SYSTEMS V-1
- A. Formaldehyde from Methanol Process Using a Metallic Silver Catalyst V-1
- B. Formaldehyde from Methanol Process Using a Metal Oxide Catalyst V-5
- C. References V-9

VI. IMPACT ANALYSIS VI-1
- A. Environmental and Energy Impacts VI-1
- B. Control Cost Impact VI-4
- C. References VI-21

VII. SUMMARY VII-1

84

APPENDICES OF REPORT 1

A. PHYSICAL PROPERTIES OF FORMALDEHYDE, METHANOL, AND PARAFORMALDEHYDE

B. AIR-DISPERSION PARAMETERS

C. FUGITIVE-EMISSION FACTORS

D. COST ESTIMATE DETAILS

E. EXISTING PLANT CONSIDERATIONS

F. LIST OF EPA INFORMATION SOURCES

TABLES OF REPORT 1

Number		Page
II-1	Formaldehyde Usage and Growth	II-2
II-2	Formaldehyde Capacity	II-4
IV-1	Uncontrolled Emissions from Metallic-Silver-Catalyst Process	IV-3
IV-2	Model Plant Storage	IV-3
IV-3	Emission Composition for Metallic-Silver-Catalyst Process	IV-4
IV-4	Uncontrolled Emissions from Metal-Oxide-Catalyst Process	IV-7
IV-5	Absorber Vent Gas Composition for Metal-Oxide-Catalyst Process	IV-8
IV-6	Absorber Vent Emission Ratios	IV-10
V-1	Controlled Emissions for Metallic-Silver-Catalyst Process	V-2
V-2	Controlled Emissions for Metal-Oxide-Catalyst Process	V-6
VI-1	Environmental Impact of Controlled Model-Plant Formaldehyde Production by Metallic-Silver-Catalyst Process	VI-2
VI-2	Environmental Impact of Controlled Model-Plant Formaldehyde Production by Metal-Oxide-Catalyst Process	VI-3
VI-3	Cost Factors Used in Computing Annual Costs	VI-5
VI-4	Control Device Cost Effectiveness for Metallic-Silver-Catalyst Process	VI-6
VI-5	Estimates of Emission Control and Reduction and Cost Effectiveness for Formaldehyde Model Plant Using a Metal Oxide Catalyst	VI-19
VII-1	VOC Emission Summary for Model Plant	VII-2
A-1	Properties of Anhydrous Formaldehyde and Methanol	A-1
A-2	Properties of Formaldehyde Solution (37 wt %)	A-1
A-3	Properties of Paraformaldehyde	A-2
B-1	Air-Dispersion Parameters for Metallic-Silver-Catalyst Process Model Plant with a Capacity of 45 Gg/yr	B-1
B-2	Air-Dispersion Parameters for Metal-Oxide-Catalyst Process Model Plant with a Capacity of 45 Gg/yr	B-2
E-1	Control Devices Currently Used by the Domestic Formaldehyde Industry	E-4

FIGURES OF REPORT 1

Number		Page
II-1	Locations of Plants Manufacturing Formaldehyde	II-6
III-1	Flow Diagram for Metallic-Silver-Catalyst Process	III-3
III-2	Flow Diagram for Metal-Oxide-Catalyst Process	III-6
VI-1	Capital Cost for Thermal Oxidation	VI-7
VI-2	Annual Cost for Thermal Oxidation	VI-8
VI-3	Cost Effectiveness for Thermal Oxidation	VI-9
VI-4	Installed Capital Cost vs Plant Capacity for Fractionator Vent Emission Controls	VI-11
VI-5	Net Annual Cost or Savings vs Plant Capacity for Fractionator Vent Emission Controls	VI-12
VI-6	Cost Effectiveness vs Plant Capacity for Fractionator Vent Emission Controls	VI-13
VI-7	Installed Capital Cost vs Plant Capacity for Formaldehyde Storage Emission Control	VI-15
VI-8	Net Annual Cost vs Plant Capacity for Formaldehyde Storage Emission Control	VI-16
VI-9	Cost Effectiveness vs Plant Capacity for Formaldehyde Storage Emission Control	VI-17
D-1	Precision of Capital Cost Estimates	D-2

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Formaldehyde production was selected for study because preliminary estimates indicated that emissions of volatile organic compounds (VOC) from the industry were high and because an increase in formaldehyde consumption was expected to continue.

Pure, dry formaldehyde is a colorless gas characterized by a pungent odor. Its stability in the gaseous state depends on its purity; however, even traces of water will cause rapid polymerization. Therefore formaldehyde is manufactured and transported only in solution or in the polymerized state. The domestic production capacity of formaldehyde is reported traditionally on the basis of a 37 wt % solution, although it is manufactured and sold in different forms, e.g., 37, 44, 50, 52, and 56 wt % solutions and as paraformaldehyde, a solid.[1] Whenever possible customers buy the high-concentration product in order to reduce freight charges.[1] Appendix A gives the pertinent physical properties of formaldehyde.

B. FORMALDEHYDE USAGE AND GROWTH

The current production capacity of formaldehyde in the United States (based on 37 wt % solution) is 4066 Gg/yr, with the 1977 production being 2750 Gg/yr, or 68% of this capacity.[1,2] Formaldehyde consumption is expected to increase at an average annual rate of 4 to 5% during 1977--1982.[1,3] At these rates production will be 85% of current capacity by 1982.

The uses of formaldehyde and their expected growth rates are given in Table II-1. The manufacture of adhesives constitutes 60% of the end use for the formaldehyde produced. The major derivatives -- urea-formaldehyde and phenol-formaldehyde resins -- are used principally in the manufacture of particle board and plywood. Thus the consumption pattern of formaldehyde depends largely on the construction industry.[3]

The manufacture of plastics accounts for approximately 10% of the formaldehyde produced. Butanediol, a derivative of formaldehyde, is used in making polybutylene terephthalate (PBT). If the use of plastic in automobile production increases

Table II-1. Formaldehyde Usage and Growth[a]

End Use	Production for 1977 (%)	Average Growth[b] for 1977--1982 (%/yr)
Urea resins	25.4	0 to 3
Phenolic resins	24.3	4 to 5
Butanediol	7.7	12
Acetol resins	7.0	9 to 10
Pentaerythritol	6.0	1 to 3
Hexamethylenetetramine	4.5	2 to 3
Melamine resins	4.2	7
Urea formaldehyde concentrates	3.6	3
Chelating agents	3.6	5
4,4'-Methylenedianiline and 4,4'-methylenediphenyl isocyanate	2.6	12 to 15
Textile treating applications	1.8	-1 to +1
Pyridine chemicals	1.3	8
Trimethylolpropane	1.3	7
Nitroparaffin derivatives	0.4	7
Other	6.3	7

[a] See ref. 1.

[b] Growth rates are rounded to the nearest 1%.

and PBT plastic is chosen as the principal material used, formaldehyde could have a growth rate of more than 10% annually for a few years.[3]

C. DOMESTIC PRODUCERS

Because most of the formaldehyde is manufactured and shipped as a solution containing 50% or more water, the distance from the producing point to the consuming point is minimized to reduce shipping costs. Therefore the industry is characterized by a large number of relatively small plants. Since more than half the formaldehyde used is in the manufacture of adhesives for wood products, the producing plants are located predominantly in the south and northwest.[3]

Sixteen producers were operating 55 formaldehyde plants at the end of 1977.[1] Table II-2 lists the producers, locations, capacities, and processes; Fig. II-1 shows the plant locations.

Formaldehyde has a tendency to polymerize on storage. When an inhibitor is added to prevent excessive polymerization at lower storage temperatures, it is usually methanol at 7 to 11% concentration. Most of the formaldehyde is sold uninhibited and must be kept warm (above 54°C) to prevent polymerization.

All the formaldehyde produced in the United States is made from methanol either by a combination oxidation-dehydrogenation process using a silver catalyst or by catalytic oxidation in the vapor phase using a metal oxide catalyst. About half the formaldehyde producers also produce methanol feedstock (Borden, Celanese, Du Pont, Georgia-Pacific, Hercules, IMC, Monsanto, and Tenneco). Reichhold is the only large producer that does not make its own methanol feedstock.[1]

Table II-2. Formaldehyde Capacity[a]

Location Key[b]	Producer	Capacity[c] (Gg/yr) Silver Process[d]	Capacity[c] (Gg/yr) Metal Oxide Process[e]
	Allied Chemical Corporation		
1A	South Point, OH	141	
	Borden, Inc.		
2A	Demopolis, AL	45	
2B	Diboll, TX	36	
2C	Fayetteville, NC	106	
2D	Geismar, LA	113	
2E	Louisville, KY	36	
2F	Sheboygan, WI	59	
2G	Fremont, CA	102	
2H	Kent, WA	36	
2I	LaGrande, OR	29	
2J	Missoula, MT	41	
2K	Springfield, OR	109	
	Celanese Chemical Company		
3A	Bishop, TX	680	
3B	Newark, NJ		53
3C	Rock Hill, SC		53
	Chembond Corporation		
4A	Springfield, OR		68
4B	Winnfield, LA		32
	Du Pont Company		
5A	Belle, WV	227	
5B	LaPorte, TX	145	
5C	Healing Springs, NC	100	
5D	Linden, NJ	73	
5E	Toledo, OH	122	
	GAF Corporation		
6A	Calvert City, KY		45
	Georgia-Pacific Corporation[f]		
7A	Albany, OR		54
7B	Columbus, OH		45[g]
7C	Coos Bay, OR		41[g]
7D	Crossett, AR	45	27
7E	Russellville, SC		113[g]
7F	Taylorsville, MS		54
7G	Vienna, GA	45	
7H	Lufkin, TX		45
	Gulf Oil Corporation		
8A	Vicksburg, MS		27
	Hercules Inc.		
9A	Louisiana, MO	77	
9B	Wilmington, NC	45	
	Hooker Chemicals and Plastics Inc.		
10A	North Tonawanda, NY	61	

Table II-2. (Continued)

Location Key[b]	Producer	Capacity[c] (Gg/yr) Silver Process[d]	Metal Oxide Process[e]
	IMC Chemical Group, Inc.		
11A	Seiple, PA	29	
11B	Sterlington, LA	14	
	Monsanto Corporation		
12A	Addyston, OH	45	
12B	Chocolate Bayou, TX	88	
12C	Eugene, OR	45	
12D	Springfield, MA	134	
	Pacific Resins & Chemicals, Inc.		
13A	Eugene, OR	43	
	Reichhold Chemicals, Inc.		
14A	Hampton, SC	23	
14B	Houston, TX		54
14C	Kansas City, KA	23	
14D	Malvern, AR		50
14E	Moncure, NC		55
14F	Tacoma, WA		22
14G	Tuscaloosa, AL	33	
14H	White City, OR		113
	Tenneco Inc.		
15A	Fords, NJ	45	39
15B	Garfield, NJ	45	
	Wright Chemical Corporation		
16A	Reigelwood, NC		
Total process capacity		3040	1026
Number of plants		35	20
Percent of total industry capacity		74.8	25.2
Capacity of total industry[h]			4066

[a] See refs. 1 and 2. [b] See Fig. II-1 for plant locations. Because of space limitations, symbols on map do not reflect precise locations. [c] Based on 37 wt % solution. [d] Silver catalyst process. [e] Mixed metal-oxide-catalyst process. [f] Capacity of Russellville, SC, plant, which came on-stream in 1975, is 113 Gg/yr [see 1976 Directory of Chemical Producers. United States of America, p. 62 in January to July Supplement, Chemical Information Services, Stanford Research Institute, Menlo Park, CA (July 1977)]. [g] Georgia-Pacific Corporation in 1979 stated their Columbus, Coos Bay, and Russellville capacities to be 32, 34, and 90 Gg/yr (per letter dated May 30, 1979, from V. J. Tretter, Georgia-Pacific, to R. T. Walsh, EPA). [h] In 1976 Rohm and Haas closed an 11-Gg/yr plant at Philadelphia, PA, and Union Carbide closed a 54-Gg/yr plant at Bound Brook, NJ.

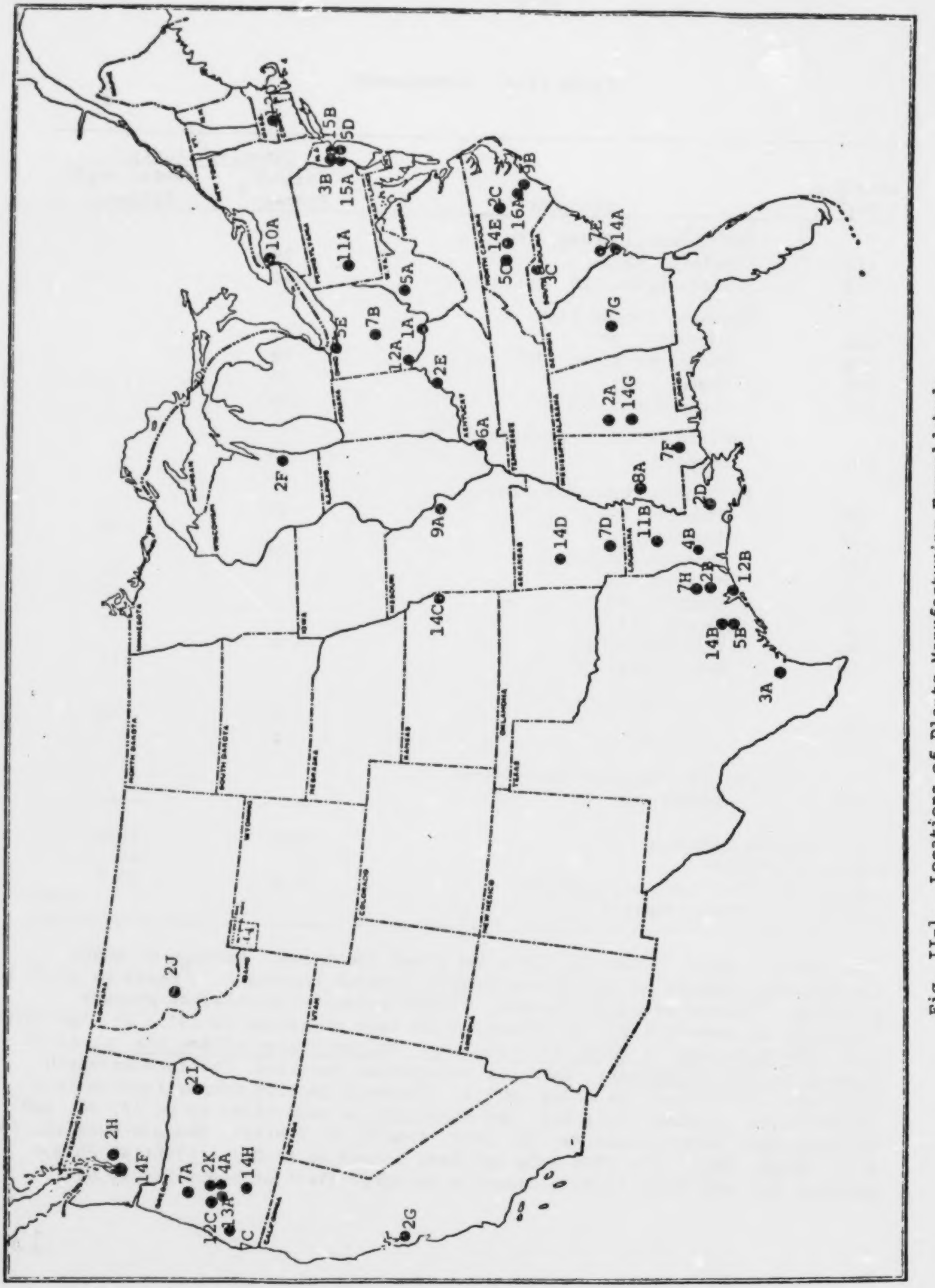

Fig. II-1. Locations of Plants Manufacturing Formaldehyde (See Table II-2 for identification of plants)

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

III. PROCESS DESCRIPTION

A. INTRODUCTION

In the United States two major processes are used in the manufacture of formaldehyde from methanol: the metallic-silver-catalyst combination dehydrogenation-oxidation process (silver process), which is used at 35 locations to produce 75% of the formaldehyde manufactured, and the metal-oxide-catalyst oxidation process (metal oxide process), which is used at 20 locations to produce 25% of the formaldehyde manufactured. The projected annual production growth for each process is 4 to 5%.[1,2]

Two gas-phase reactions are employed to form formaldehyde from methanol:

Reaction 1 -- Dehydrogenation

$$\underset{\text{(methanol)}}{CH_3OH} \longrightarrow \underset{\text{(formaldehyde)}}{HCHO} + \underset{\text{(hydrogen)}}{H_2}$$

Reaction 2 -- Oxidation

$$\underset{\text{(methanol)}}{CH_3OH} + \underset{\text{(oxygen)}}{\tfrac{1}{2}O_2} \longrightarrow \underset{\text{(formaldehyde)}}{HCHO} + \underset{\text{(water)}}{H_2O}$$

The silver process involves the dehydrogenation of methanol (reaction 1) followed by oxidation of a portion of the hydrogen evolved to form water, or a combination of dehydrogenation and oxidation of methanol (reactions 1 and 2). The metal oxide process involves oxidation of methanol by reaction 2.[3]

The major difference between the two processes is the amount of air mixed with the methanol before conversion. Since air and methanol form explosive mixtures at concentrations of approximately 6 to 37 vol % of methanol in air, the air/methanol input must be controlled.[4] The metallic-silver-catalyst dehydrogenation-oxidation processes maintain an excess of methanol, and methanol concentrations are above the explosive range, whereas the metal-oxide-catalyst oxidation processes use an excess of air so that the methanol concentrations are below the lower limits of the explosive range. Off-gas from the metallic-silver-catalyst process contains 18 to 20% hydrogen and less than 1% oxygen.[4] Off-gas from the metal-oxide-catalyst process contains unreacted oxygen and no appreciable concentration of hydrogen.

With the metallic-silver-catalyst process the excess methanol must be separated to meet customer specifications. With the metal-oxide-catalyst process the large excess of air requires a larger compressor and the process equipment must be larger to handle the added air volume.

B. METALLIC-SILVER-CATALYST PROCESS

1. Process Description

The process flow diagram shown in Fig. III-1 represents a typical continuous metallic-silver-catalyst process.

The incoming air (Stream 1) is washed with caustic to remove traces of sulfur dioxide, hydrogen sulfide, and other impurities that act as catalyst poisons. The air is then compressed to 143 kPa and passed through a vaporizer column, where it is heated and saturated with methanol vapor (Stream 2). The heated air and methanol vapor must comprise more than 37 vol % methanol in order to be above the high explosive limit of the methanol.

The mixture (Stream 3) then enters a battery of converters. Approximately 80% of the methanol feed is reacted for a per-pass conversion ratio of 0.80. The converter temperature is maintained at approximately 635°C (ref. 5) by heat generated by the oxidation of a portion of the hydrogen evolved and/or by methanol oxidation. The hot effluent gases (Stream 4) are quickly cooled to prevent decomposition of the formaldehyde formed. Cooling is accomplished by heat interchange with the feed mixture in the vaporizer and by then introducing the gas into the primary absorber.

The primary-absorber liquid is an aqueous solution of formaldehyde and methanol. A portion of this liquid is withdrawn from the bottom of the absorber column and recirculated to the top. The remainder (Stream 5) is pumped to the product fractionation column. The uncondensed vapors and noncondensable gases (Stream 6) are withdrawn from the top of the primary-absorber column and fed to a secondary absorber.

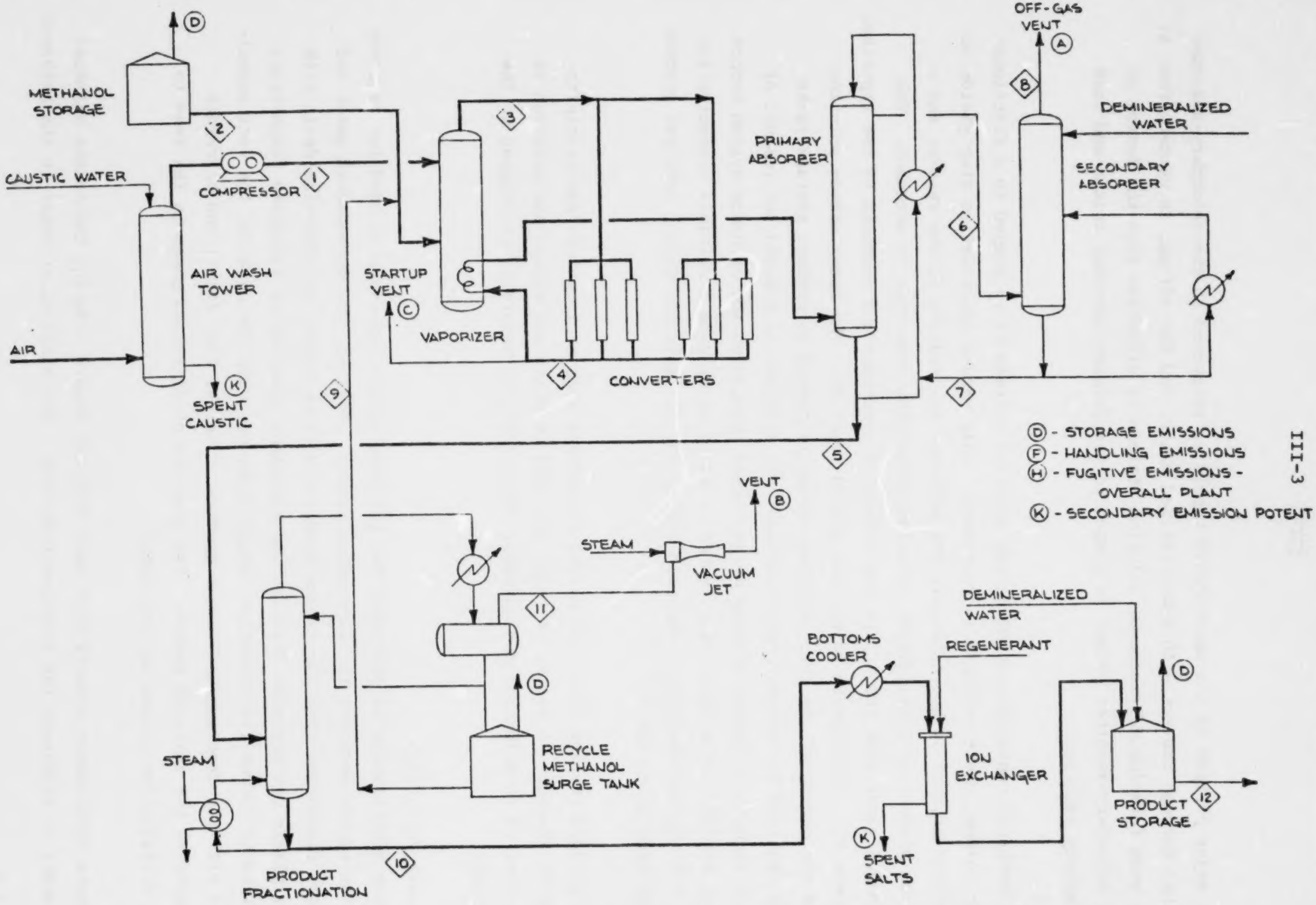

Fig. III-1. Flow Diagram for Uncontrolled Model Plant Producing Formaldehyde from Methanol with the Metallic-Silver-Catalyst Process

The major portion of the uncondensed vapors is recovered in the secondary-absorber column through contact with demineralized water, and the off-gas is vented (Vent A). The weak formaldehyde/methanol solution (Stream 7) withdrawn from the bottom of the secondary-absorber column is pumped to the primary-absorber column and used as makeup solution.

The methanol-containing formaldehyde solution (Stream 5) is pumped to a fractionation column, where methanol is recovered. This vacuum distillation step yields an overhead product of approximately 99% methanol for recycle to the reactor and a bottom product of formaldehyde solution containing less than 1% methanol. The methanol vapor from the top of the column is condensed and recycled to the vaporizor (Stream 9). Uncondensed vapors are vented (Vent B). The formaldehyde solution from the bottom of the fractionation column is pumped to product storage tanks. When required by customer specifications the solution is treated for removal of trace amounts of formic acid by being passed through an ion exchange system before being stored. As a final step, water is added to provide a suitable concentration for storage and shipping. Reported yields for the metallic-silver-catalyst process range from 83 to 92%.[1,3--5]

All product storage tanks are heated to prevent polymer formation and precipitation in storage. A series of tanks are used to blend and adjust the solution to the desired formaldehyde and methanol concentrations before it is shipped to the customer.

2. Process Variations

Vacuum distillation is described for the model-plant process step used for recovery of the excess methanol in the product stream. However, the uncondensed gases and vapors discharged from the vacuum producer must be vented or otherwise dealt with. Many plants use pressure distillation equipment operated at increased temperature, instead of vacuum fractionation, which dispenses with the need for the vent associated with the fractionator vacuum producer (Vent B, Fig. III-1) and therefore eliminates the emission source. The quantity of dissolved gases in the feed to the distillation column is very small.

Process development efforts have been directed toward reducing the excess methanol in order to eliminate the fractionation step. The addition of water to the methanol to form a feed mixture containing 30 to 50 vol % water can produce a product containing 7 to 8 wt % methanol.[5] This concentration of methanol is suitable for some markets.[5]

Many approaches have been taken by the various plants to improve efficiency for heat utilization. In some plants heat from the reactor is used to heat the methanol distillation reboiler or to generate steam to drive the fractionation-column vacuum pump.[5]

C. METAL-OXIDE-CATALYST PROCESS

1. Process Description

The process flow diagram shown in Fig. III-2 represents a typical continuous metal-oxide-catalyst process. The catalyst system most often used is ferric molybdate.

Incoming air (Stream 1) may be washed with caustic solution in a packed tower to remove dust and trace impurities. The air is then compressed, along with the recycle gas (Stream 5) to 143 kPa. Recycle of a portion of the oxygen-lean vent gases lowers the oxygen content of the air feed stream to below 10.9%.[5] This reduces the explosion hazard of the feed mixture and increases the equipment output by reducing the amount of excess air required to keep the methanol concentration below the low explosive limit.[5]

A portion of the air is passed through the vaporizer column, where it is saturated with methanol (Stream 2). The methanol-saturated air is then mixed with the remaining air and preheated by heat exchange with the product gas leaving the converter. The feed gas mixture (Stream 3) then enters the converter. Conversion ratios of 97% are obtained. The converter, heated by the exothermic oxidation reaction, is maintained at 345°C (ref. 5) by boiling heat transfer fluid in the reactor shell. Steam is generated by condensation of the heat-transfer fluid vapors.

The product gas (Stream 4) is cooled by heat exchange with the feed gas mixture and then quenched in the absorber column. The formaldehyde and methanol are removed from the gas stream by absorption in the aqueous solution. The unabsorbed gases and vapors exit at the top of the absorber column. A portion (60 to 80%) of this gas is recycled (Stream 5) and the remaining gas is vented. The product

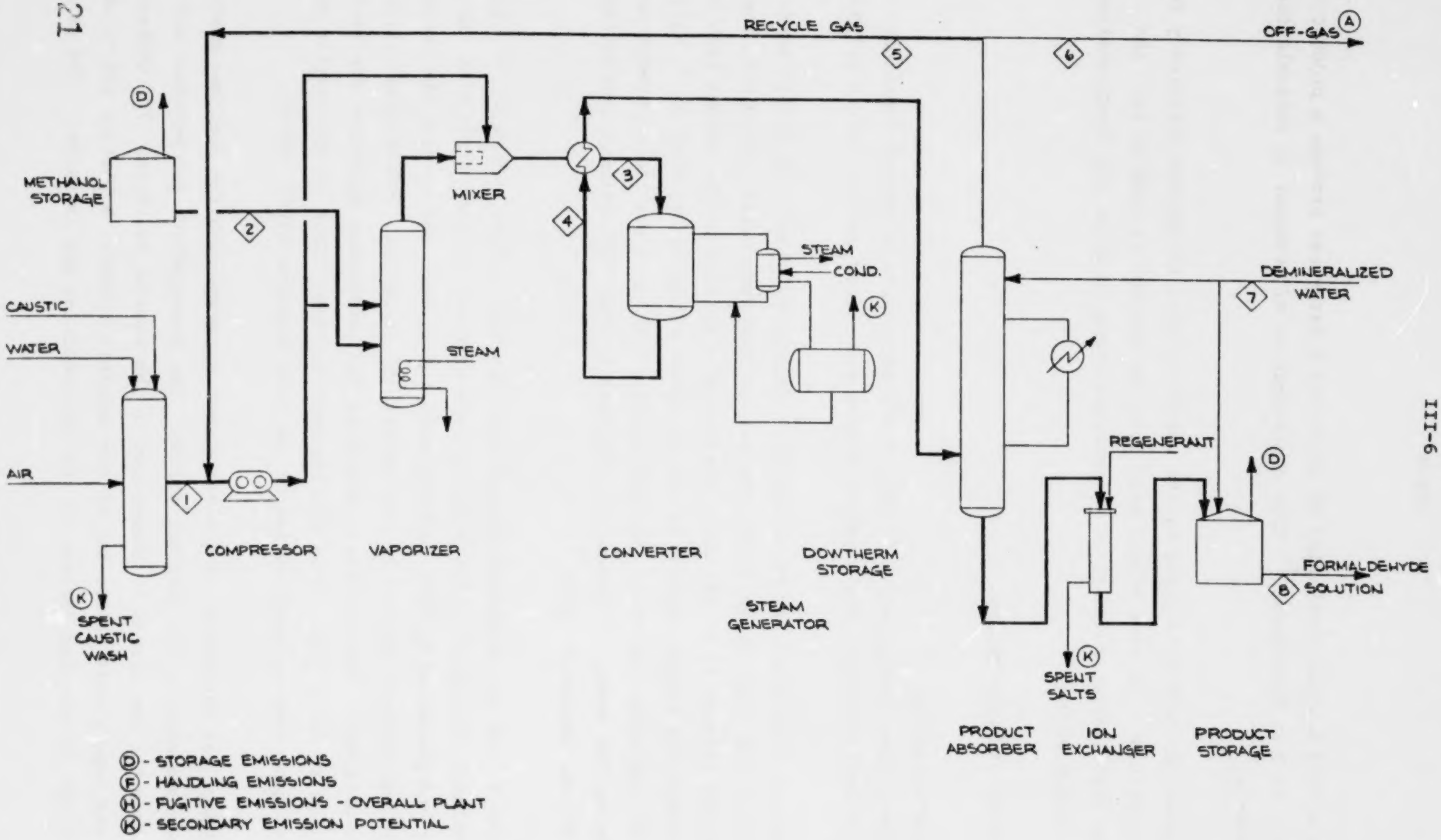

Fig. III-2. Flow Diagram for Uncontrolled Model Plant Producing Formaldehyde from Methanol with the Metal-Oxide-Catalyst Process

solution drawn from the bottom of the absorber column contains approximately 0.8% methanol and 0.005% formic acid. The solution is usually treated in an ion exchange system to reduce the acidity and is then stored. As a final step water is added to provide a suitable concentration for storage and shipping. Process yields of 91 to 93% are reported for the metal-oxide-catalyst process.[1,5]

The formaldehyde yield from the metal-oxide-catalyst process is higher than that from the metallic-silver-catalyst process and the metal-oxide-catalyst process is simpler, because methanol distillation is not required. The equipment costs for the metal-oxide-catalyst process are greater because of the large volume gas streams; also, because of a lower concentration of formaldehyde in the product gas stream, the absorber column diameter is larger and the operating temperature is lower than those used with the metallic-silver-catalyst process.[5]

2. Process Variations

The industry makes use of various catalyst compositions and methods and extent of heat recovery. Otherwise, the processes used are basically similar. Many older plants do not recycle a portion of the absorber-column vent gas. For these plants the vent gas volume and the ratio of volatile organic compounds emitted per unit of product produced are increased.[6]

The oxide catalyst is not susceptible to poisoning by traces of sulfides in the air feed; thus many plants filter the incoming air rather than utilizing caustic scrubbers.

D. OTHER PROCESSES

1. Formaldehyde by Partial Oxidation of Methane

Considerable research has been devoted to production of formaldehyde directly from methane. The process is more complex and requires a higher capital investment than do processes utilizing methanol. Commercial attempts to produce formaldehyde from natural gas or methane has had limited success and the process currently is not used in the United States.[5]

2. Formaldehyde by Partial Oxidation of Light Hydrocarbons

Higher hydrocarbons, such as ethane, propane, or butane, may also be oxidized to formaldehyde. This process was used originally by the Celanese Corporation at their large Bishop, Texas, plant but has recently been replaced by the metallic-silver-catalyst process using methanol as the feedstock. Because of the cost of light hydrocarbons it is doubtful that any new facility in the United States will again utilize this process.[6]

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IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

The process emissions estimated for the formaldehyde model plants are based on the emissions reported in responses to EPA's requests for information from selected companies, on EPA emission testing data, and on data obtained during visits to Celanese and Borden formaldehyde production plants (see Appendix E). Also used in sizing and design of the model plants were data from the EPA studies, SRI reports, formaldehyde data compiled by J. F. Walker, and an understanding of the process chemistry and yields.

A. FORMALDEHYDE FROM METHANOL PROCESS USING A METALLIC SILVER CATALYST

1. Model Plant

The model plant* for this study has a capacity of 45 Gg/yr, based on 8760 hr of operation per year.** Although not an actual operating plant, it is typical of many plants built recently. The plant utilizes the model metallic-silver-catalyst process (Fig. III-1) and best fits today's formaldehyde manufacturing and engineering technology for that process.

Typical raw-material, intermediate, and product-storage tank capacities were estimated for the 45-Gg/yr model plant. Storage tank requirements are given in Sect. IV.A.2.e. Estimates of potential fugitive sources, based on data from existing plants, are given in Sect. IV.A.2.d.[1--3] Characteristics of the model plant that are important in air-dispersion modeling are shown in Appendix B.

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*See p. I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

2. Sources and Emissions

Uncontrolled emission rates and sources for the metallic-silver-catalyst process are summarized in Table IV-1 and are described below. The process emission rates are based on emission data from existing plants. Potential storage, handling, fugitive, and secondary emissions were calculated from characteristics of the plant and from data on existing plants (see Table IV-2).

a. Absorber Vent -- The absorber vent (Vent A, Fig. III-1) is the principal source of emissions from the formaldehyde production plant. The volatile organic compounds (VOC) in the vent gas include unreacted methanol, formaldehyde, methyl formate, and methylal (see Table IV-3). Also included in the vent gas are hydrogen, methane, carbon monoxide, carbon dioxide, nitrogen, water vapor, and a small amount of unreacted oxygen. The composition of the absorber vent varies somewhat with the catalyst's age and activity.[4] The average emission during normal operation is given in Table IV-1.

b. Product Fractionator Vent -- A product fractionator operated under vacuum is used to separate and recover unreacted methanol from the product stream. A steam ejector or vacuum pump is employed to produce the vacuum required. Emissions from this source (Vent B) include methanol vapor, formaldehyde, water vapor, and a small amount of inert gases (see Table IV-3).

c. Intermittent Air Emissions -- The formaldehyde plant is normally operated at design conditions to achieve highest yields. It is shut down when product inventories are filled. Since the metallic-silver-catalyst process operates above the upper explosive limit of methanol, the plant startup procedure must be handled carefully. Unstable conditions are often encountered and explosions can occur in the methanol vaporizer and the reactor. Various startup procedures are used in the industry. Usually during startup the output from the reactor is vented until stable operation is achieved and an acceptable yield ratio is obtained. The flow is then switched into the absorber. The total startup time is 1 to 2 hr.[2] The reactor feed rate varies as the startup proceeds. Initially the reactor produces mainly carbon

Table IV-1. Total VOC from Uncontrolled Emissions Produced by Formaldehyde Metallic-Silver-Catalyst Process in a Model Plant

Emission Source	Stream Designation (Fig.III-1)	Emissions	
		Ratio (g/kg)[a]	Rate (kg/hr)
Absorber	A	4.73	24.5
Product fractionator	B	1.58	8.2
Intermittent[b]	C	0.11	0.28
Methanol storage	D	0.08	0.43
Formaldehyde storage	D	0.03	0.2
Handling	F	0.01	0.1
Fugitive	H	1.08	5.7
Secondary	K	0.01	0.03
Total		7.63	39.44

[a] g of total VOC per kg of 37% formaldehyde solution produced.

[b] Average rate for entire year, based on 8 startups per year and flow of one-half the normal rate during startup.

Table IV-2. Model Plant Storage

Content	Tank Size (m³)	No. of Tanks Required	Turnovers Per Year	Bulk Liquid Temperature (°C)
		Metallic-Silver-Catalyst Process		
Methanol (feed)	190	2	68	25
Formaldehyde	190	4	45	54
Methanol (recycle)	4	1	*	38
		Metal-Oxide-Catalyst Process		
Methanol (feed)	190	2	65	25
Formaldehyde	190	4	45	54

* Surge tank.

Table IV-3. Emission Composition for Model Metallic-Silver-Catalyst Process[a]

	Emissions			
	Absorber Vent		Fractionator Vent	
Component	Composition (wt %)	Ratio[b] (g/kg)	Composition (wt %)	Ratio[b] (g/kg)
VOC	0.75	4.73	83.16	1.58
Formaldehyde	(0.06)	(0.36)	(17.49)	(0.33)
Methanol	(0.14)	(0.89)	(65.67)	(1.24)
Methyl formate	(0.36)	(2.27)		
Methylal	(0.19)	(1.20)		
Combustible gases	2.38	14.97		
Hydrogen	(1.69)	(10.59)		
Methane	(0.28)	(1.77)		
Carbon monoxide	(0.41)	(2.61)		
Other gases	93.96	590.23	0.94	0.02
Oxygen	(0.42)	(2.63)		
Nitrogen	(86.64)	(544.23)		
Carbon dioxide	(6.90)	(43.37)		
Water vapor	2.91	18.25	15.90	0.3013
Total	100.00	628.17	100.00	1.90

[a] Emission rates are based on emission data from existing plants; see Appendix E.

[b] g of emission per kg of 37 wt % formaldehyde solution produced.

dioxide and water vapor. As the temperature rises, the formaldehyde yield increases, thereby enlarging the amount of VOC in the gas vented. The average annual emission calculated from this source (see Table IV-1) is based on an average of eight startups per year and a flow of one-half the normal rate during startup.

d. Fugitive Emissions -- Process pumps, valves, and circulating process cooling water are potential sources of fugitive emissions. The model plant is estimated to have 13 pumps, 214 process valves, and 6 relief valves handling VOC.[1--3] An estimated 6.5 liters of cooling water per kg of product produced is circulated through the cooling tower. Fugitive emission factors from Appendix C were applied to determine the fugitive emissions shown in Table IV-1.

e. Storage and Handling Emissions -- Emissions result from the storage and handling of methanol and formaldehyde. Sources for the model plant are shown in Fig. III-1 (Source D). Storage tank conditions for the model plant are given in Table IV-2. The emissions in Table IV-1 are based on fixed-roof tanks, half full, and a diurnal temperature variation of 11.1°C and were calculated based on the emission equations from AP-42.[5] However, calculated breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overpredicts emissions.[6]

Since uninhibited formaldehyde polymerizes at a low temperature, concentrated solutions (over 30% HCHO) must be kept warm.[7] Therefore the model-plant formaldehyde storage tanks are maintained at above 54°C. Since these tanks are temperature controlled, breathing losses are negligible and emissions given are based on working losses only.

Emissions from the loading of formaldehyde solution into trucks and tank cars were calculated with the equations from AP-42, with submerged-fill-pipe loading assumed to be used.[8] These emissions are also included in Table IV-1.

f. Secondary Emissions -- Secondary VOC emissions can result from the handling and disposal of process-waste liquid streams. The potential sources (Source K) that exist for the model plant are ion exchange system regeneration and blowdown water from the cooling and air-wash towers. The calculated total secondary VOC emission from these sources is given in Table IV-1. Calculations are based on wastewater data reported by industry and the assumptions that the ion exchange system is operated for 10% of the production and that 5% of the VOC contained in the wastewater evaporates before treatment.

B. FORMALDEHYDE FROM METHANOL PROCESS USING A METAL OXIDE CATALYST

1. Model Plant

The model plant for this study is based on the metal-oxide-catalyst process utilizing vent gas recycling (Fig. III-2). This model process best fits today's formaldehyde manufacturing and engineering technology for utilizing a metal oxide catalyst. The model plant has a capacity of 45 Gg/yr based on 8760 hr of operation per year.

Typical raw-material and product-storage tank capacities were estimated for the 45-Gg/yr model plant. Storage tank requirements are given in Sect. IV.B.2.e. Estimates of potential fugitive sources, based on data from existing plants, are given in Sect. IV.B.2.d.[1--3] Characteristics of the model plant that are important in air-dispersion modeling are given in Appendix B.

2. Sources and Emissions

Uncontrolled emission rates and sources for the metal-oxide-catalyst process are summarized in Table IV-4 and are discussed below. Process emission rates are based on emission data from existing plants. Potential storage, handling, fugitive, and secondary emissions were calculated from model-plant characteristics and data from existing plants.

Since the process operates below the explosive limit with an excess of air, unstable conditions during startup are easily prevented. Venting of the reactor during startup is not required.

a. Absorber Vent -- The product absorber vent (Vent A, Fig. III-2) is the main source of emissions from the formaldehyde production plant. The VOC components in the vent gas include methanol, formaldehyde, and dimethyl ether (Table IV-5). Also included in the vent gas are carbon monoxide, carbon dioxide, nitrogen, oxygen, and water vapor.

Table IV-4. Total VOC Uncontrolled Emissions for Formaldehyde Produced by Metal-Oxide-Catalyst Process in a Model Plant

Source	Stream Designation (Fig.III-1)	Emissions	
		Ratio (g/kg)[a]	Rate (kg/hr)
Absorber	A	3.15	16.3
Methanol storage	D	0.08	0.44
Formaldehyde storage	D	0.03	0.2
Handling	F	0.01	0.1
Fugitive	H	0.74	3.7
Secondary	K	0.05	0.2
Total		4.06	20.7

[a] g of total VOC per kg of 37% formaldehyde solution produced.

Table IV-5. Absorber Vent Gas Composition for Model Metal-Oxide-Catalyst Process[a]

Component	Emissions: Composition (wt %)	Emissions: Ratio[b] (g/kg)
VOC	0.27	3.15
Formaldehyde	(0.04)	(0.44)
Methanol	(0.16)	(1.93)
Dimethyl ether	(0.07)	(0.79)
Other gases	95.45	1124.39
Oxygen	(7.91)	(93.20)
Nitrogen	(86.09)	(1014.02)
Carbon dioxide	(0.19)	(2.28)
Carbon monoxide	(1.26)	(14.89)
Water vapor	4.28	50.37)
	100.00	1177.91

[a] Emission rates are based on emission data from existing plants; see Appendix E.

[b] g of emission per kg of 37 wt % formaldehyde solution produced.

The emission composition and flow rates are especially affected by the percent of absorber gas recycled. By recycling a portion of the oxygen-lean vent gas, the oxygen concentration in the reactor feed mixture can be reduced, making it possible for the concentration of methanol to be increased without an explosive mixture being formed. This reduces the volume of reaction gases and thus reduces equipment size and horsepower required to drive the compressor. Recycling reduces the emission rate and enhances the reactor equilibrium to produce a higher yield.[9]

The effect of recycling on absorber vent emissions can be seen by the comparison of absorber vent gas composition for recycling and nonrecycling operations given in Table IV-6.

Other variables that affect the absorber vent emissions are catalyst formulation, catalyst age, absorber temperature, and strength of formaldehyde produced.[10] The catalyst formulation can affect the overall process yield and thus the amount and type of by-products or emissions produced. Also, product yields tend to decrease as the catalyst ages. Lowering the absorber temperature increases its efficiency and thus lowers the VOC emissions from the absorber. As the strength of the formaldehyde produced increases, the partial pressure due to the formaldehyde increases, thus increasing the relative amount of formaldehyde in the vent emission.

The model-plant average absorber vent emission during normal operation is given in Table IV-4. A recycle rate of 63 vol % for the product absorber vent gas was calculated based on emissions data.

b. Fugitive Emissions -- Process pumps and valves are potential sources of fugitive emissions. The model plant is estimated to have 8 pumps, 176 process valves, and 4 relief valves handling VOC. An estimated 6.5 liters of cooling water per kg of product produced is circulated through the cooling tower. Fugitive emission factors from Appendix C were applied to determine the fugitive emissions shown in Table IV-4.

c. Storage and Handling Emissions -- Emissions result from the storage and handling of methanol and formaldehyde. Sources for the model plant are shown in Fig. III-2 (Source D). Storage tank conditions for the model plant are given in Table IV-2. The emissions in Table IV-4 are based on fixed-roof tanks, half full, and a diurnal temperature variation of 11.1°C and were calculated based on the emission equations

Table IV-6. Absorber Vent Emission Ratios for Recycled Vent Gas vs Nonrecycled Vent Gas for Model Metal-Oxide-Catalyst Process

	Emission Ratio (g/kg)[a]	
Component	Recycled Vent Gas	Nonrecycled Vent Gas
Total VOC[b]	3.2	12.7
Other[c]	1174.8	5440.0
Total	1178.0	5452.7

[a] g of total VOC per kg of 37% formaldehyde solution produced.

[b] Includes formaldehyde, methanol, and dimethyl ether.

[c] Includes nitrogen, oxygen, carbon dioxide, carbon monoxide, and water.

from AP-42.[5] However, the breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing-loss equation overpredicts emissions.[6]

Since uninhibited formaldehyde polymerizes at low temperature, concentrated solutions (over 30% HCHO) must be kept warm.[7] Consequently the model-plant formaldehyde storage tanks are maintained above 54°C. Breathing losses are negligible because the tank temperature is controlled. Emissions therefore are based on only working losses.

Emissions from the loading of formaldehyde solution into trucks and tank cars were calculated with the equations from AP-42.[8] These emissions are included in Table IV-4.

d. Secondary Emissions -- Secondary VOC emissions can result from the handling and disposal of process-waste liquid streams. The potential sources (Source K) that exist for the model-plant are ion exchange system regeneration, blowdown water from the cooling and air-wash towers, and emissions from the heat-transfer fluid system vent. The total secondary VOC emission from these sources is given in Table IV-4. Emissions were calculated based on wastewater data reported by industry and the assumptions that the ion exchange system is operated for 100% of the production and that 5% of the VOC contained in the wastewater evaporates before treatment.

C. REFERENCES*

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an *additional* reference is required for only a certain *portion* of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

V. APPLICABLE CONTROL SYSTEMS

A. FORMALDEHYDE FROM METHANOL PROCESS USING A METALLIC SILVER CATALYST

1. Absorber Vent

Thermal oxidation can be used effectively to control the emissions from the absorber vent. The vent stream is rich in hydrogen gas and contains other clean-burning hydrocarbons. The heating value of the gas is high enough to self-sustain combustion. If the gas is fired with a nominal amount of supplemental fuel to maintain stable combustion conditions, heat can be recovered from the flue gas. An emission reduction efficiency of greater than 99% can be obtained with this system. Thermal oxidizer systems and efficiencies are discussed in a separate EPA control device evaluation report.[1]

Control of model-plant absorber vent emissions (see Table V-1) is by a thermal oxidizer coupled with a waste heat boiler to generate low-pressure steam. Supplemental fuel (natural gas) and the vent gas are fired through separate burners. The vent gas can also be effectively oxidized in a conventional steam generator through use of a specially designed burner unit.[2] When the vent gas is used as supplemental fuel, its combustion in the boiler is essentially complete, with an expected emission reduction efficiency of greater than 99%.

Flaring of the vent gases has been practiced at some plants in the past; flaring, however, does not allow recovery of heat. A flare incorporating appropriate safety features could be used for controlling the absorber vent emissions and startup emissions if heat recovery is not to be considered. Flares and the use of emissions as fuel are the subject of a separate EPA control device evaluation report.[3]

Catalytic oxidation would not provide additional advantage over thermal oxidation, since the gas mixture has a high heating value. However, if surplus heat availability negates the value of steam production, catalytic oxidation may be a viable option.

2. Product Fractionator Vent

The model-plant fractionator vent emissions are controlled by recycle. A surface condenser is used to condense the vapor issuing from the steam jet ejector. The condensate, containing approximately 95% of the VOC, is returned to the secondary

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Table V-1. Total Controlled VOC Emissions for Model-Plant Formaldehyde Production Using a Metallic Silver Catalyst

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emissions	
				Ratio[a] (g/kg)	Rate (kg/hr)
Absorber	A	Thermal oxidation	99	0.047	0.24
Production fractionator	B	Recycle	100	Negligible	Negligible
		Water scrubber	95	0.079	0.41
Methanol storage	D	Internal-floating-roof tank	85	0.012	0.06
Formaldehyde storage	D	Vent scrubber	96	0.003	0.01
Handling	F	Vapor recovery	96	0.001	0.005
Fugitive	H	Repair and maintenance	81	0.21	1.09
Secondary	K	None	—	0.006	0.03
Total (product fractionator emissions recycled)			96	0.28	1.44

[a] g of total VOC per kg of 37% formaldehyde solution produced.

[b] Average rate for entire year, based on 8 startups per year.

absorber as a part of the makeup water. The remainder of the VOC is recovered by returning the uncondensed gases to the air-compressor suction manifold, thus obtaining essentially 100% reduction in emissions. The uncondensable portion of the gases will be subsequently emitted from the absorber vent. These gases contain essentially no VOC.

An alternate method of control could be achieved by directing the uncondensed gases from the separator to the proposed absorber-vent thermal oxidizer. With this option a total VOC reduction efficiency of 99.95% would be achieved, with 95% of the formaldehyde and methanol in the emission stream recovered.

A mechanical vacuum pump could be installed to replace the steam jet ejector. The gases and vapors exhausted by the pump would be returned to the air-compressor suction manifold, thus achieving total recycle.

A water scrubber could be used as an alternate control option, with a resultant removal efficiency of greater than 95% based on average scrubber efficiencies reported by scrubber manufacturers.* The discharge water can be used as makeup for the product absorber, thus allowing the methanol and formaldehyde scrubbed from the vent gas to be recovered.

A final control option would be to combine the emissions from the fractionator vent with the absorber-vent emissions going to the proposed thermal oxidizer. An overall reduction of 99% would be achieved.

3. Intermittent Air Emissions

The model plant is assumed to operate at one-half the normal production rate during startup. Since a relatively small quantity of VOC is emitted during the early startup phase, it is normally vented to the atmosphere until the emission composition reaches a steady state above the flammable range. If a suitable flare system is available at a nearby production unit on the plant site, the startup emissions could possibly be routed to the existing flare. Suitable safety precautions, such as purging with natural gas, would be required. The capital cost of a flare system may be less than that for thermal oxidation; however, the cost effectiveness of a flare is poor because heat recovery is precluded.

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*Information contained in various catalogs and/or sales brochures.

A multipurpose thermal oxidizer designed to handle the normal absorber-vent flow and the converter startup flow would not be feasible because of the design conditions and the infrequent occurrence of the startup emissions. At peak flow during the startup period the heat produced by the quantity of combustible gases discharged from the converter is approximately 3 times that of the heat capacity of the proposed absorber-vent thermal oxidizer. The specific heat of the startup mixture reaches a level of more than twice that of the normal absorber-vent gas. The duct work from the reactor to the thermal oxidizer and the burner internals would have to be designed to accommodate the hot gases that are discharged directly from the reactor, or some arrangement would have to be included to cool the gas. Explosive mixtures could inadvertently occur during startup, with the thermal oxidizer acting as a potential source of ignition. During the latter phase of the startup a source of ignition would not be needed, because the reactor temperature would be above the autoignition temperature of the mixture. The system therefore would have to be designed for the peak startup duty with turndown capability for the normal vent flow. More sophisticated controls would be required to accommodate the varying composition and quantity of these gases during the startup period, and explosion vents would have to be added to the system.

4. Fugitive Sources

Controls for fugitive sources are discussed in a separate EPA report.[4] Fugitive emissions from equipment, pumps, valves, and the process water cooling tower can be controlled by an appropriate leak-detection system, plus repair and maintenance as needed. Controlled fugitive emissions calculated with the factors given in Appendix C are included in Table V-1. The factors are based on the assumption that major leaks are detected and repaired.

5. Storage and Handling Sources

a. Methanol Storage -- Internal-floating-roof tanks* are commonly used for control of storage-tank VOC emissions and are used in the model plant for methanol storage control. The controlled methanol emissions given in Table V-1 were calculated by assuming that a contact-type internal floating roof with secondary seals will reduce fixed-roof-tank emissions by 85%.[5]

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*Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed. (fixed-roof tanks with internal floating device to reduce vapor loss).

b. Formaldehyde Storage -- Formaldehyde storage emissions are controlled in the model plant by a vent scrubber. A portion of the fresh feed water going to the secondary absorption tower is used as the scrubber medium. The water, after passing through the vent scrubber, is used for product dilution or is returned to the absorption tower as makeup. The tank emissions recovered are thus returned to the process. A reduction efficiency of 96%, typical of an average scrubber system, was used to calculate the controlled emissions given in Table V-1.

c. Other Tank Emissions -- The methanol recycle tank is small and has low emissions and is uncontrolled in this model plant.

d. Handling -- Emissions occurring during the loading of tank cars and tank trucks are controlled by a vapor recovery system. The vapors displaced are returned to the proposed formaldehyde tank-vent scrubber system. The controlled handling emissions given in Table V-1 were calculated on the assumption of 96% reduction efficiency.

6. Secondary Emissions

Secondary emissions result from evaporation of VOC contained in aqueous effluent from the plant. Control of secondary emissions is discussed in a separate EPA report.[6] No control system has been identified for the secondary emissions from the model plant.

7. Current Emission Control

The control devices being used by domestic formaldehyde producers are discussed in Appendix E.

B. FORMALDEHYDE FROM METHANOL PROCESS USING A METAL OXIDE CATALYST

1. Absorber Vent

Thermal oxidation controls the absorber-vent emissions from the model plant. A VOC reduction of greater than 99% can be achieved and was used to calculate the controlled emission rate given in Table V-2. Heat from the oxidizer flue gases can be recovered either by generating steam by a waste heat boiler or by preheating the incoming vent gas and combustion air with recuperative heat exchangers.

Table V-2. Total Controlled VOC Emissions for Model-Plant Formaldehyde Production Using a Metal Oxide Catalyst

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emissions	
				Ratio[a] (g/kg)	Rate (kg/hr)
Absorber	A	Thermal oxidation	99	0.032	0.16
Methanol storage	D	Covered floating-roof tank	85	0.014	0.07
Formaldehyde storage	D	Vent scrubber	96	0.003	0.01
Handling	F	Vapor recovery	96	0.001	0.005
Fugitive	H	Repair and maintenance	74	0.19	0.98
Secondary	K	None	—	0.047	0.24
Total			93	0.287	1.47

[a] g of total VOC per kg of 37% formaldehyde solution produced.

The vent gas is largely inert, thus requiring that supplemental fuel be fired through a separate burner. Thermal oxidizer systems and efficiencies are discussed in a separate EPA control device evaluation report.[1]

A larger portion of the heat can be recovered by generation of steam than by recuperative heating, making the steam generation option more attractive from an energy standpoint. Since the metal-oxide-catalyst process itself produces an excess of steam, recuperative heating may be attractive for plants having no use for the steam. Recuperative heating greatly reduces the quantity of fuel required to maintain combustion conditions.

One manufacturer reported using a water scrubber to control the absorber-vent emissions. The performance of the scrubber, however, is hampered by the insoluble nature of the dimethyl ether contained in the vent stream. For the model plant the overall VOC removal efficiency for this system would be 74%. However, wastewater from the scrubber is discharged to wastewater treatment. Thus the secondary emissions due to evaporation of the absorbed VOC would increase the rate of secondary emissions by 350%.

2. Fugitive Sources

Controls for fugitive sources are discussed in a separate EPA report.[4] Control of emissions from pumps and valves can be attained by an appropriate leak detection system followed by repair maintenance. Controlled fugitive emissions have been calculated with the factors given in Appendix C and are included in Table V-2. The factors are based on the assumption that major leaks are detected and repaired.

3. Storage and Handling Sources

a. Methanol Storage -- Internal-floating-roof tanks are commonly used for control of storage-tank VOC emissions and are used in the model plant for methanol storage control. The controlled methanol emissions given in Table V-2 were calculated by assuming that a contact-type internal floating roof with secondary seals will reduce fixed-roof-tank emissions by 85%.[5]

b. Formaldehyde Storage -- A vent scrubber system is used to control the formaldehyde storage-tank vent emissions. A portion of the fresh feed water going to the secondary absorption tower is used as the scrubber medium. The scrubber discharge water is returned to the absorption tower or is used for product dilution. The tank emissions recovered are thus returned to the process. A reduction efficiency of 96% was used to calculate the controlled emissions given in Table V-2.

c. Handling -- Vapors displaced while tank cars and tank trucks are being loaded are controlled by a vapor recovery system. A vent line is attached to the vessel being filled and the vapors are returned to the proposed formaldehyde tank vent-scrubber system. The controlled handling emissions given in Table V-2 were calculated on the assumption of 96% reduction efficiency for the scrubber system.

4. Secondary Emissions

Sources of secondary emissions from a plant using the metal-oxide-catalyst process are from evaporation of VOC contained in aqueous wastes going to wastewater treatment and from the vent on the heat transfer system. No control system has been identified for the secondary emissions from the model plant. Control of secondary emissions is discussed in a separate EPA report.[6]

5. Current Emission Control

The control devices being used by domestic formaldehyde producers are discussed in Appendix E.

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VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

1. Formaldehyde Model Plants

The environmental impact of reducing total VOC emissions by application of the described control systems to the model plants (Table VI-1) would be 330 Mg/yr for the metallic-silver-catalyst process and 170 Mg/yr for the metal-oxide-catalyst process. By incorporating thermal oxidation with heat recovery 6892 MJ/hr of energy is recovered by the metallic-silver-catalyst process and 7447 MJ/hr is recovered by the metal-oxide-catalyst process. Deducting the energy required to operate all emission controls, including thermal oxidizer auxiliary fuel, gives a net energy gain of 5286 MJ/hr for the metallic-silver-catalyst process and a net consumption of 2751 MJ/hr for the metal-oxide-catalyst process.

2. Metallic-Silver-Catalyst Process

Table VI-1 shows the environmental impact of reducing total VOC emissions by application of the described control systems to the model plant. The addition of emission controls under option A will result in a reduction of 96%, or 330 Mg of VOC emissions per year, and a net recovery of energy of 5286 MJ/hr.

A typical uncontrolled plant using the metallic-silver-catalyst process will require about 198 kJ of energy per kg of formaldehyde solution produced.[1] The potential net energy savings is 1029 kJ/kg. Thus with heat recovery applied, a typical plant could produce 831 kJ of excess energy per kg of formaldehyde solution produced, which is equivalent to a production of 4269 MJ/hr for the model plant. If heat recovery were not incorporated, the total energy consumption of the plant with the emission controls applied would be 2569 MJ/hr.

3. Metallic-Oxide-Catalyst Process

Table VI-2 shows the environmental impact of reducing total VOC emissions by application of the described emission control systems to the model plant. The controls described will reduce total VOC emissions by 94%, or 171 Mg/yr.

Three types of thermal oxidation systems are described: oxidation with conventional heat recovery (generation of steam), oxidation with recuperative heat

Table VI-1. Environmental Impact of Controlled Model-Plant Formaldehyde Production by Metallic-Silver-Catalyst Process

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	Total VOC Emission Reduction (Mg/yr)
Absorber	A	Thermal oxidation	99	212.4
Product fractionator	B	Recycle process	100	71.5
		Water scrubber*	95	67.9
Methanol storage	D	Internal-floating-roof tank	85	3.2
Formaldehyde storage	D	Vent scrubber	96	1.4
Handling	F	Vapor recovery	96	1.0
Fugitive	H	Repair and maintenance	81	40.6
Secondary	K	None		
Total (product fractionator emissions recycled)			96	330.1

*Alternate system

Table VI-2. Environmental Impact of Controlled Model-Plant Formaldehyde Production by Metal-Oxide-Catalyst Process

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	
			(%)	(Mg/yr)
Absorber	A	Thermal oxidation	99	141.6
Methanol storage	D	Internal-floating-roof tank	85	3.2
Formaldehyde storage	D	Vent scrubber	96	1.4
Handling	F	Vapor recovery	96	1.0
Fugitive	H	Repair and maintenance	74	23.8
Secondary	K	None	—	—
Total			94	171.0

recovery (preheating of the vent gas and combustion air), and oxidation without heat recovery. With conventional heat recovery the net energy consumption for all controls would be 2728 MJ/hr. With recuperative heat recovery the net energy consumed would be 3878 MJ/hr and without heat recovery would be 10,156 MJ/hr.

A typical uncontrolled plant using the metal-oxide-catalyst process produces a net excess of exportable energy in the form of low-pressure steam at the rate of 232 kJ per kg of formaldehyde solution produced.[1] The emission controls described for conventional heat recovery consume 531 kJ of energy per kg of formaldehyde solution produced. The net energy consumed by the model plant would be 299 kJ per kg of formaldehyde solution produced.

B. CONTROL COST IMPACT

Estimated costs and cost-effectiveness data for control of VOC emissions resulting from the production of formaldehyde are given in this section. Details of the model plants (Figs. III-1 and III-2) are given in Sects. III and IV. Cost estimate calculations are included in Appendix D.

Capital cost estimates, based on December 1979 costs, represent the total investment required for purchase and installation of all equipment and material needed for a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the costs of formaldehyde production lost during installation or startup, research and development, or land acquisition.

Bases for the annual cost estimates for the control alternatives include utilities, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors used are itemized in Table VI-3. Recovery credits are based on the raw-material market value for the material being recovered.[2] Annual costs are for a 1-year period beginning December 1979.

1. Metallic-Silver-Catalyst Process

a. Absorber Vent (Thermal Oxidizer) -- The cost of installing a thermal oxidizer system with heat recovery to control VOC emissions from the model-plant absorber

Table VI-3. Cost Factors Used in Computing Annual Costs

Utilities	
Cooling water	\$0.026/m^3 (\$0.10/M gal)
Electricity	\$8.33/GJ (\$0.03/kWh)
Natural gas	\$1.90/GJ (\$2.00/$\bar{\text{M}}$ Btu)
Steam	\$5.50/Mg (\$2.50/$\bar{\text{M}}$ Btu)
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital
Capital recovery, 18% (10 yr life @ 12% int.)	
Taxes, insurance, administration charges, 5%	
Recovery credits*	
Energy	\$1.90/GJ (\$2.00/$\bar{\text{M}}$ Btu)
Methanol	\$0.17/kg
Formaldehyde (raw-material value)	\$0.18/kg

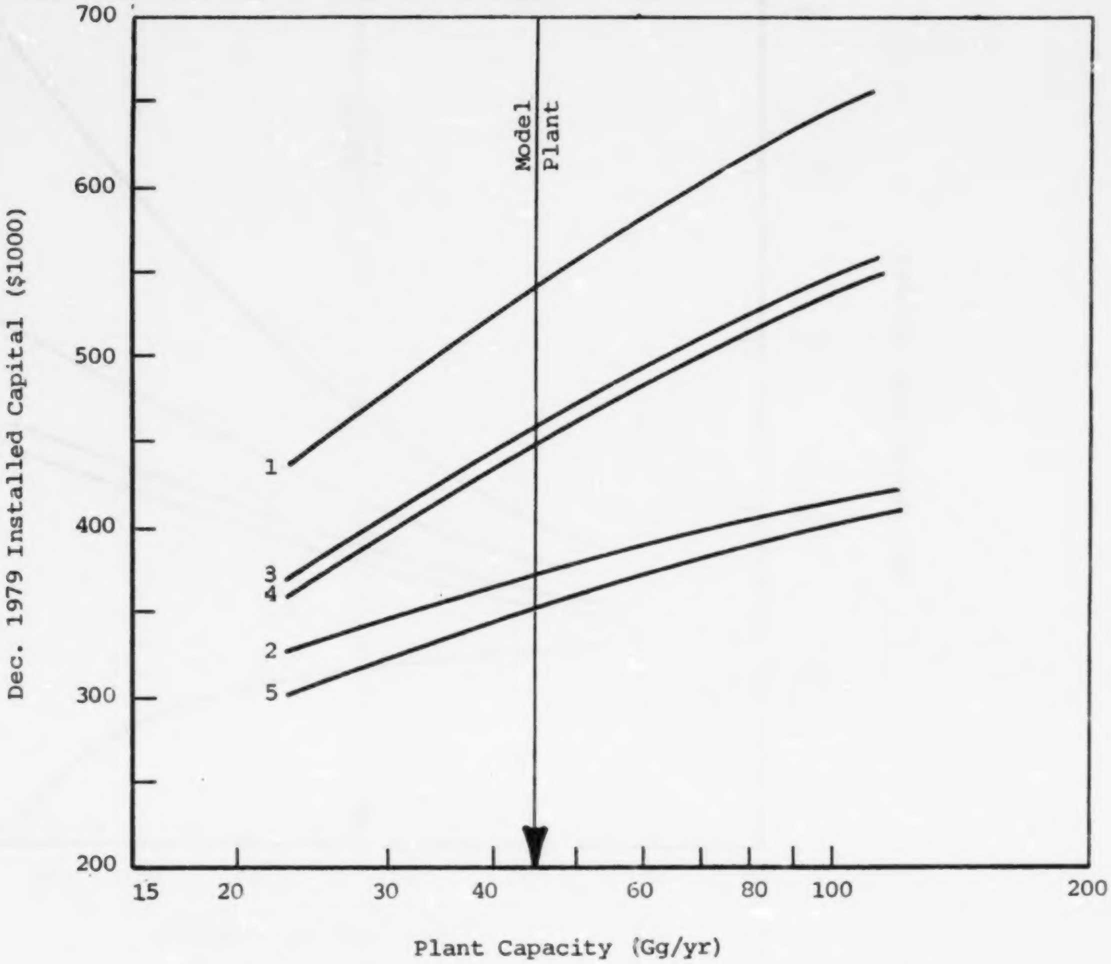
*The values used for methanol and formaldehyde solution were taken from Chemical Marketing Reporter, ref. 2.

Table VI-4. Estimates of Emission Control and Reduction and Cost Effectiveness for Formaldehyde Model Plant by Metallic-Silver-Catalyst Process

Emission Source	Control	Total Installed Capital Cost (X 1000)	Annual Operating Cost (X 1000)					Total VOC Emission Reduction (Mg/yr)	Total VOC Cost Effectiveness (per Mg)
			Fixed Cost	Utilities	Manpower	Recovery Credit	Net		
Product absorber vent	Thermal oxidation								
	No heat recovery	$370	$107	$43	$18	$ 0	$168	212.4	$ 791
	With heat recovery	540	157	43	36	(132)[a]	104	212.4	489
Product fractionation vent	Recycle condenser	47	14	0.5	b	(11.8)	2.7	71.5	35
	Scrubber	40	12	b	3.6	(11.7)	3.9	67.9	57
Formaldehyde storage and handling	Vent scrubber	49	14	b	3.6	(0.4)	17.2	2.4	7,167

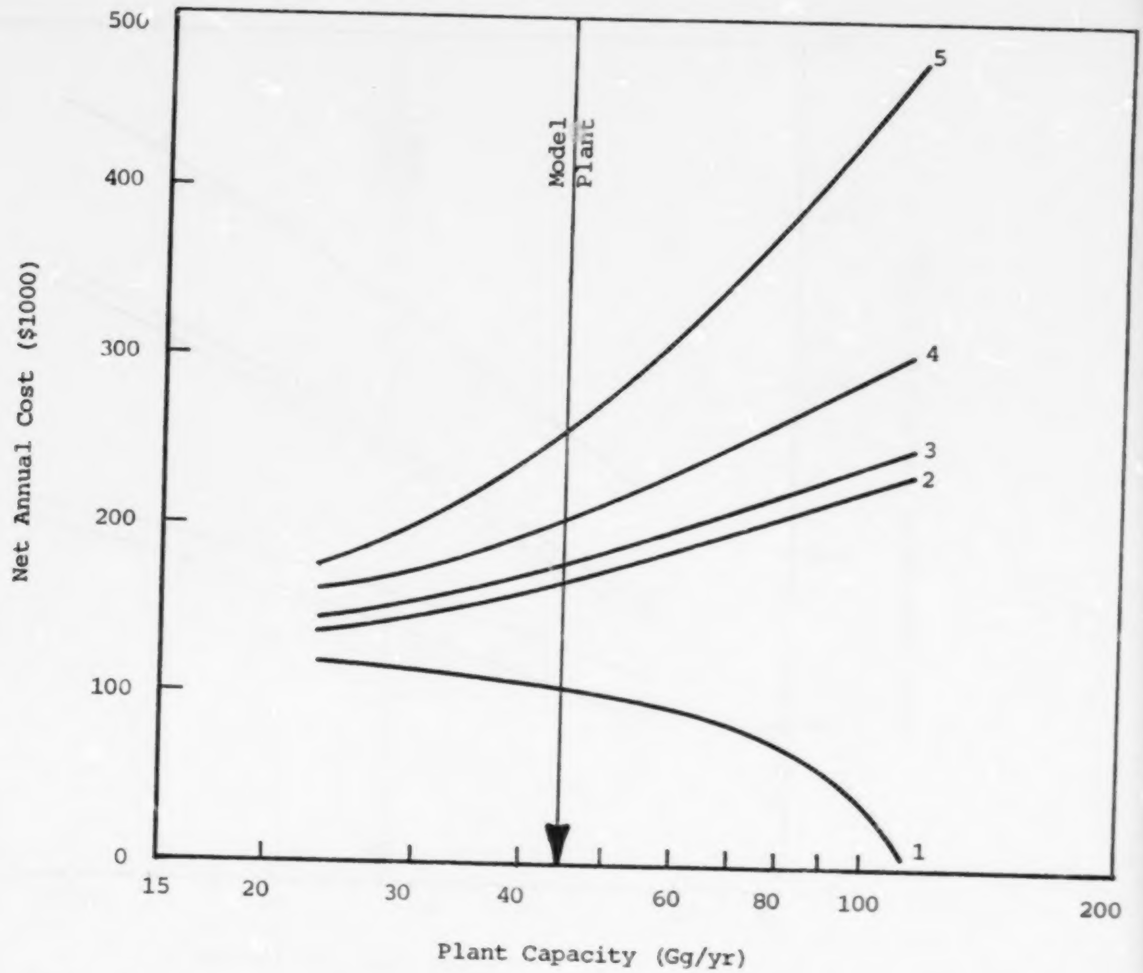
[a] Values in parentheses in these columns represent savings.

[b] Negligible.



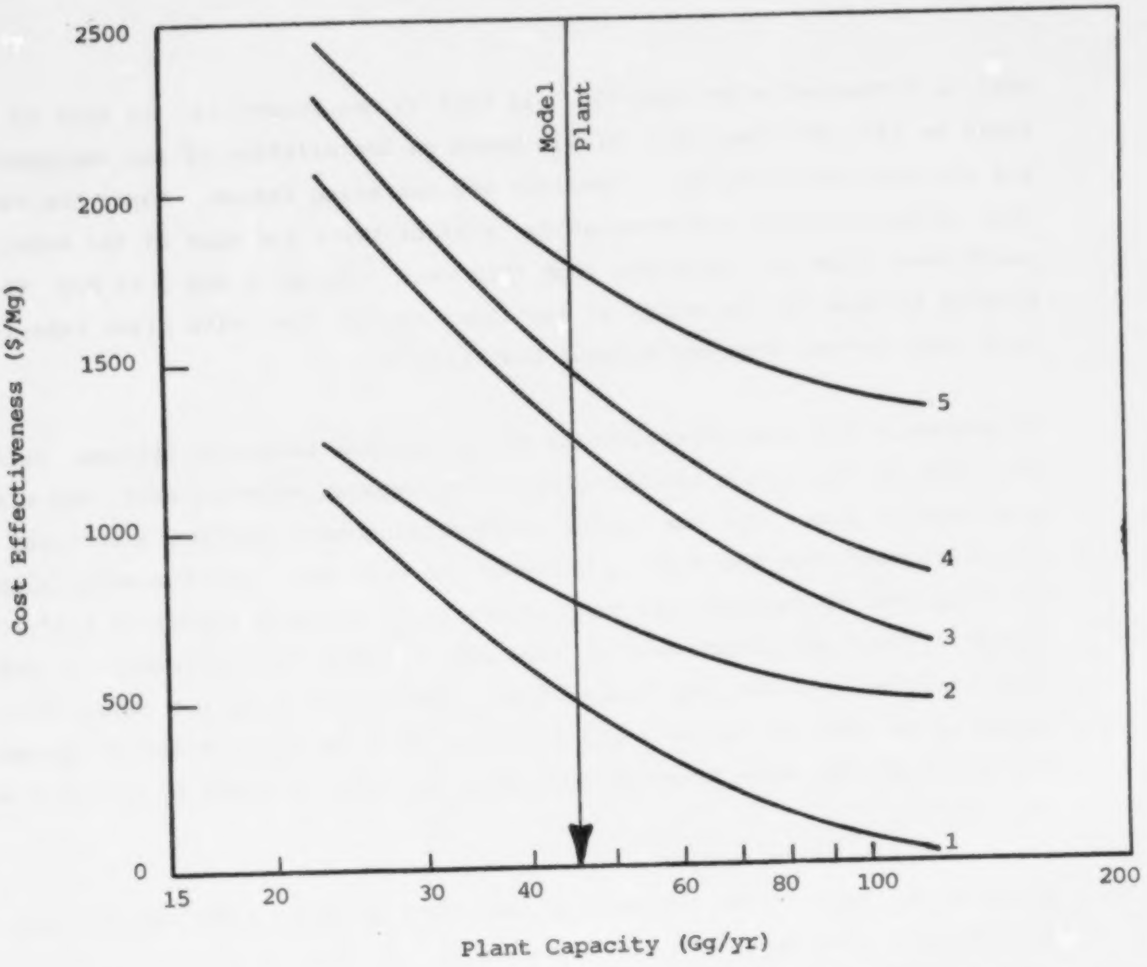
(1) Thermal oxidizer with conventional heat recovery, silver catalyst process
(2) Thermal oxidizer without heat recovery, silver catalyst process
(3) Thermal oxidizer with recuperative heat recovery, metal oxide process
(4) Thermal oxidizer with conventional heat recovery, metal oxide process
(5) Thermal oxidizer without heat recovery, metal oxide process

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Emission Control by Thermal Oxidation



(1) Thermal oxidizer with conventional heat recovery, silver catalyst process
(2) Thermal oxidizer without heat recovery, silver catalyst process
(3) Thermal oxidizer with recuperative heat recovery, metal oxide process
(4) Thermal oxidizer with conventional heat recovery, metal oxide process
(5) Thermal oxidizer without heat recovery, metal oxide process

Fig. VI-2. Net Annual Cost or Savings vs Plant Capacity for Emission Control by Thermal Oxidation



(1) Thermal oxidizer with conventional heat recovery, silver catalyst process
(2) Thermal oxidizer without heat recovery, silver catalyst process
(3) Thermal oxidizer with recuperative heat recovery, metal oxide process
(4) Thermal oxidizer with conventional heat recovery, metal oxide process
(5) Thermal oxidizer without heat recovery, metal oxide process

Fig. VI-3. Cost Effectiveness vs Plant Capacity for Emission Control by Thermal Oxidation

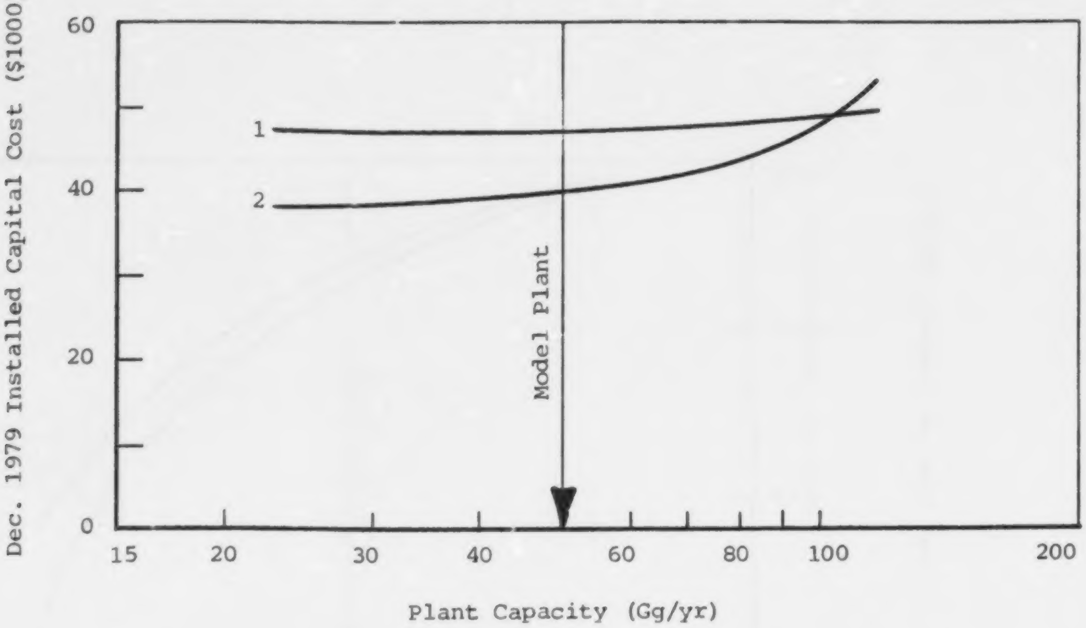
vent is estimated to be $540,000. If heat is not recovered, the cost of the system would be $370,000 (see Table VI-4), based on installation of the equipment, piping, and controls necessary for a complete and operating system. Since the vent gas rate varies directly with production, a plant twice the size of the model plant would have twice the emissions from this vent. Curves 1 and 2 of Fig. VI-1 were plotted to show the variation of installed capital cost with plant capacity for oxidation systems with and without heat recovery.

To determine the cost effectiveness of the thermal oxidation systems, estimates were made of the direct operating cost, the capital recovery cost, and miscellaneous capital costs; for the system incorporating heat recovery a recovery credit was calculated from the heating value of the vent gas. For the model plant recovering heat by conventional heat recovery the recovery credit is $132,000/yr, resulting in a net annual cost of $104,000. Without heat recovery the net annual cost would be $168,000 (see Table VI-4). The variation of net annual cost with plant capacity is shown by curves 1 and 2 of Fig. VI-2 for both oxidation systems. The variation of cost effectiveness with plant capacity is shown by curves 1 and 2 of Fig. VI-3.

b. Fractionator Vent -- The two options described in Sect. V for controlling the fractionator-vent emissions are discussed below:

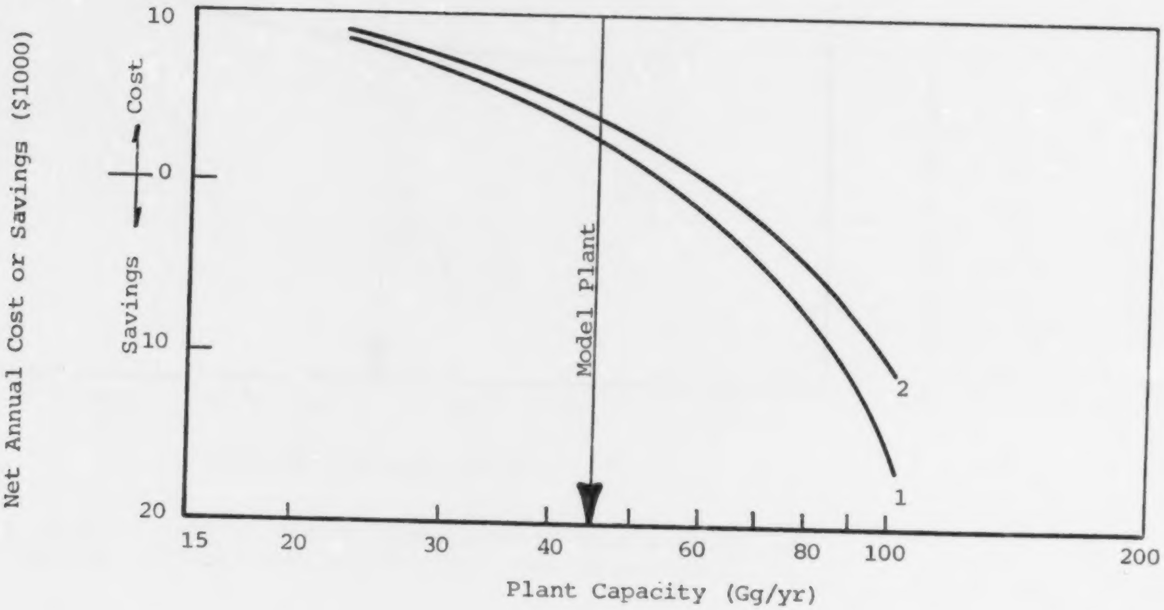
Recycle -- The emissions from the product fractionator vent are controlled by recycling the vapors back to the process. The installed capital cost of the vacuum jet condenser system for the model plant is estimated to be $47,000 (see Table VI-4). The variation of the estimated installed cost of the recycling system with plant capacity is shown by curve 1, Fig. VI-4. These estimates are based on installation of a water-cooled condenser and drum separator and include the cost of all piping and controls required for a complete and operating system. Recycling the fractionator emissions results in a net annual operating cost of $2500. Curve 1 of Fig. VI-5 shows the variation of net annual cost with plant capacity. The cost effectiveness of the system results in a cost of $35 per Mg of VOC emission removed. The variation of cost effectiveness with plant capacity is given by curve 1 of Fig. VI-6.

Scrubber -- A water scrubber unit is installed for control of emissions from the product fractionation vent. Scrubber discharge water is used as makeup water for the product absorber. The installed capital cost of the complete scrubber system



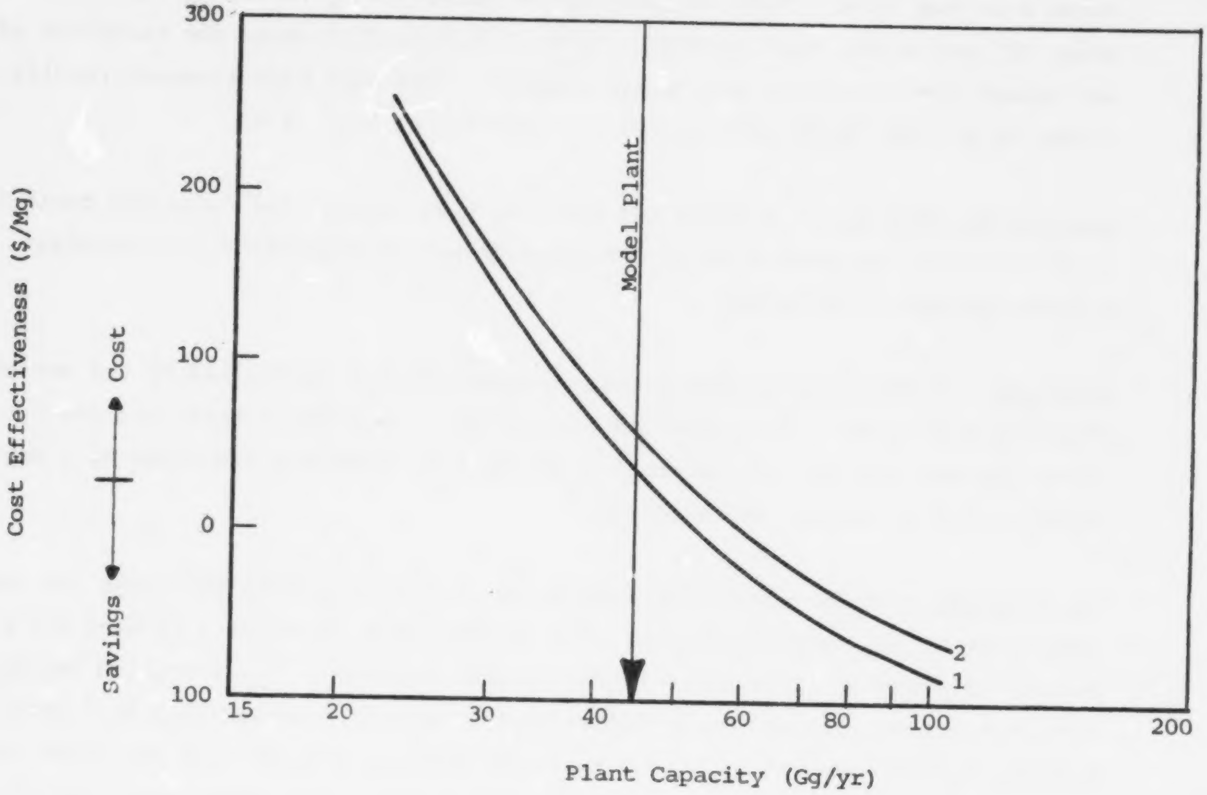
(1) Fractionator jet/condenser system, silver catalyst process
(2) Fractionator vent scrubber, silver catalyst process

Fig. VI-4. Installed Capital Cost vs Plant Capacity for Fractionator Vent Emission Controls



(1) Fractionator jet/condenser system, silver catalyst process
(2) Fractionator vent scrubbing, silver catalyst process

Fig. VI-5. Net Annual Cost vs Plant Capacity for Fractionator Vent Emission Controls



(1) Fractionator jet/condenser system, silver catalyst process
(2) Fractionator vent scrubber, silver catalyst process

Fig. VI-6. Cost Effectiveness vs Plant Capacity for Fractionator Vent Emission Controls

for the model plant is estimated to be $40,000 (see Table VI-4). The variation of the estimated cost of the scrubber system with plant capacity is shown by curve 2 of Fig. VI-4. With recovery of the emissions by recycle of the scrubber water the net annual cost is 3900. Curve 2 of Fig. VI-5 shows the variation of net annual operating cost with plant capacity. The cost effectiveness results in a cost of $57 per Mg of VOC removed (see curve 2 of Fig. VI-6).

c. Storage and Handling -- Storage and handling cost impacts for emissions control resulting from the production of formaldehyde by the metallic-silver-catalyst process are described below:

Methanol -- Model-plant methanol storage emissions are controlled by the use of floating-roof tanks. The installed capital cost, net annual cost, and cost-effectiveness data for new internal-floating-roof tanks are discussed in a separate report covering storage and handling.[3]

Formaldehyde -- Model-plant formaldehyde storage and handling emissions are controlled by a vent scrubber system. The scrubber discharge water is used for production dilution or is recycled to the product absorber. The installed capital cost, net annual cost, and cost-effectiveness data for installation of a vent scrubber system complete with vent manifold, piping, and controls are given in Table VI-4. The variation of installed capital cost, net annual cost, and cost effectiveness with plant capacity is shown by Fig. VI-7, Fig. VI-8, and Fig. VI-9, respectively. For the model plant the cost effectiveness of the system is $7167 per Mg of VOC emissions removed.

e. Fugitive Sources -- A control system for fugitive sources is defined in Appendix C. Fugitive emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry are discussed in a separate report.[4]

f. Secondary Sources -- No control system has been identified for the secondary emissions from the model plant. Secondary emissions and their control are covered by a separate EPA report.[5]

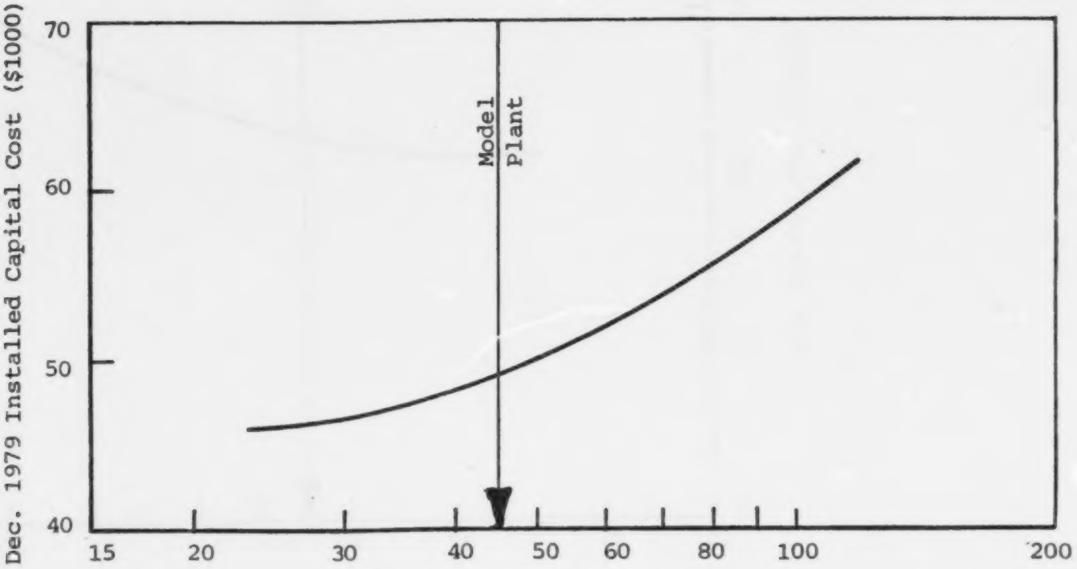


Fig. VI-7. Installed Capital Cost vs Plant Capacity for Formadlehyde Storage Emission Control

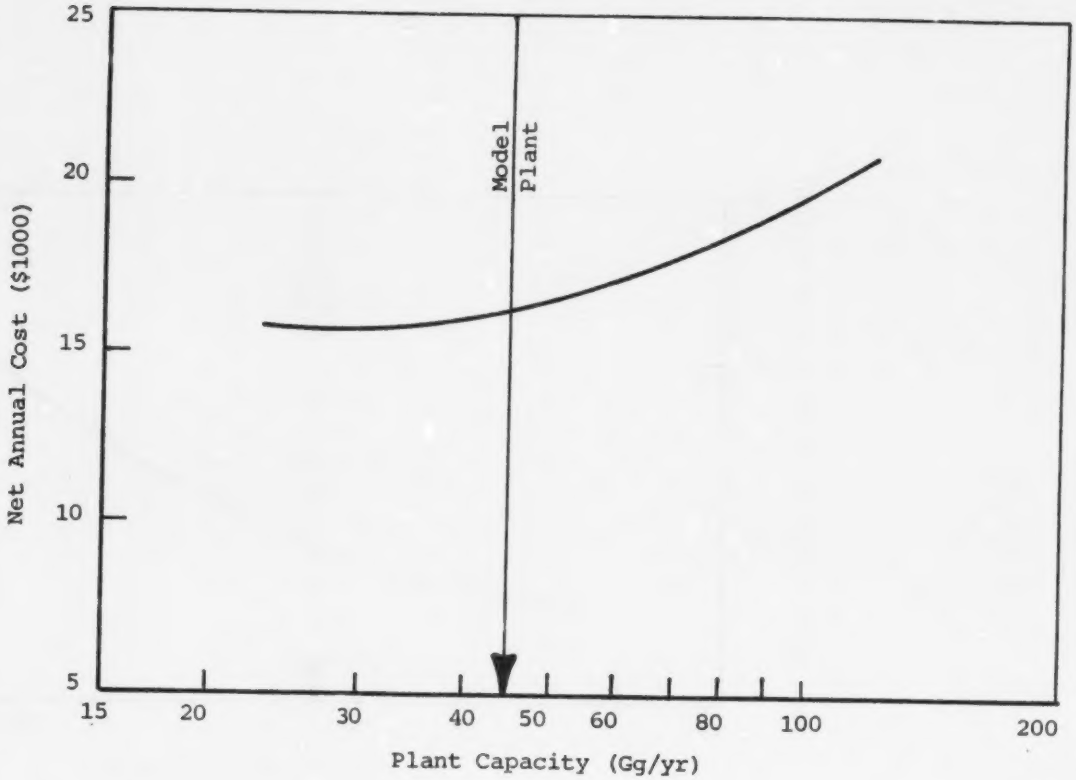


Fig. VI-8. Net Annual Cost vs Plant Capacity for Formaldehyde Storage Emission Control

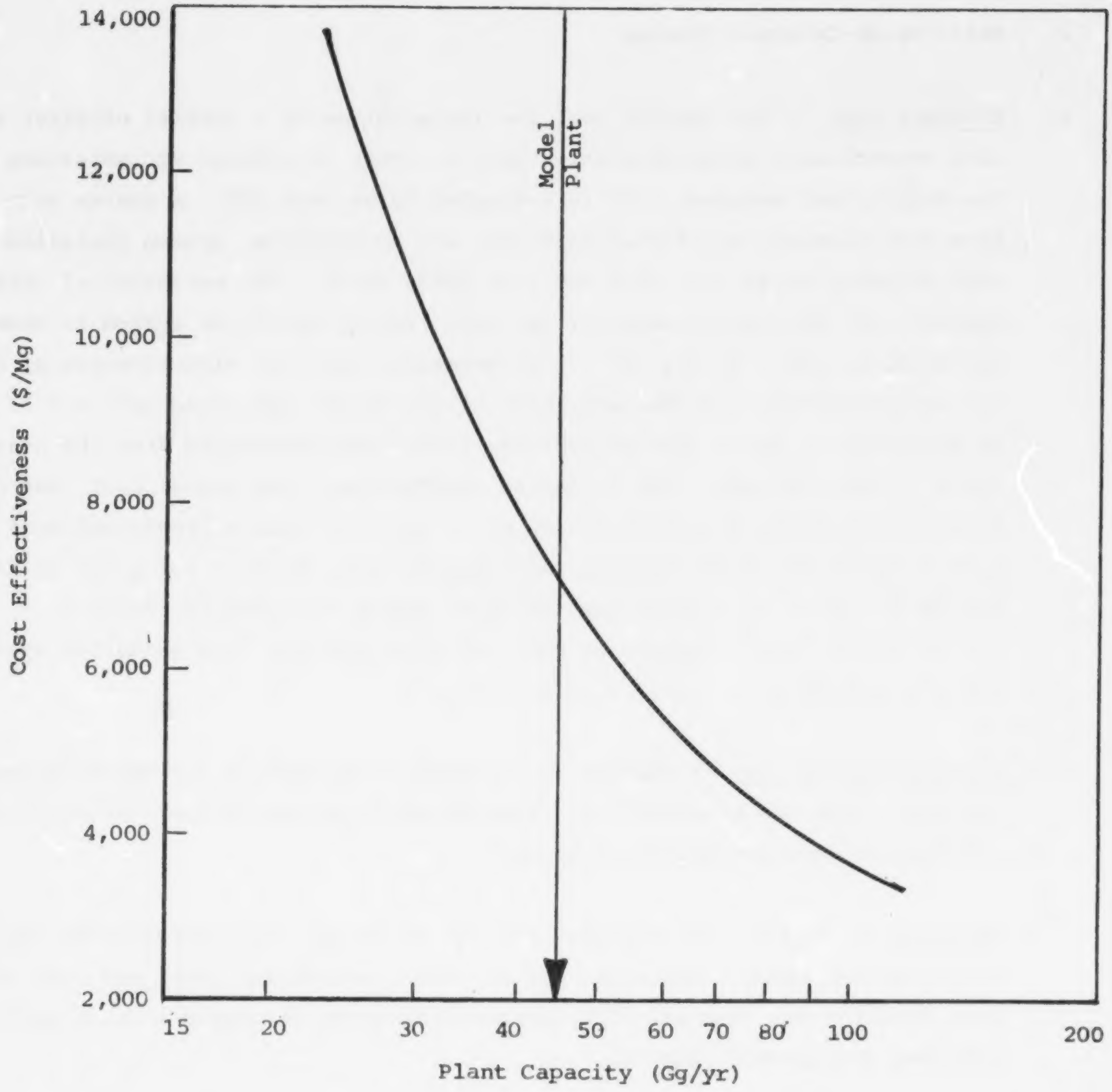


Fig. VI-9. Cost Effectiveness vs Plant Capacity for Formaldehyde Storage Emission Control

2. Metal-Oxide-Catalyst Process

a. Absorber Vent -- The capital cost for installation of a thermal oxidizer system with conventional steam-generation heat recovery to control VOC emissions from the model-plant absorber vent is estimated to be $448,000. A system with recuperative heat recovery would cost $459,000, and an oxidation system installed without heat recovery would cost $350,000 (see Table VI-5). The variation of installed capital cost with plant capacity for each type of oxidation system is shown by curves 3, 4, and 5 of Fig. VI-1. To determine the cost effectiveness of each oxidation system, estimates were made of the direct operating cost and of capital recovery costs, and a capital recovery credit was calculated from the heating value of the vent gas. The installed capital cost, net annual cost, and cost-effectiveness data for installation of an oxidizer with conventional heat recovery, with recuperative heat recovery, and without heat recovery are given in Table VI-5. The variation of net annual cost for each system is shown by curves 3, 4, and 5 of Fig. VI-2. The variation of cost effectiveness for each oxidation system is shown by curves 3, 4, and 5 of Fig. VI-3.

b. Storage and Handling -- Storage and handling cost impacts for emission control resulting from the production of formaldehyde from methanol by the metal-oxide-catalyst process are discussed below:

Methanol -- Model-plant methanol storage emissions are controlled by the use of floating-roof tanks. Installed capital cost, net annual cost, and cost-effectiveness data for new internal-floating-roof tanks are discussed in a separate report covering storage and handling.[3]

Formaldehyde -- Model-plant formaldehyde storage and handling emissions are controlled by a vent scrubber system. The scrubber discharge water is used for product dilution or is recycled to the product absorber. The installed capital cost, net annual cost, and cost-effectiveness data for installation of a vent scrubber system complete with vent manifold, piping, and controls are given in Table VI-5. The variation of installed capital cost, net annual cost, and cost effectiveness with plant capacity is shown by Fig. VI-7, Fig. VI-8, and Fig. VI-9, respectively.

Table VI-5. Estimates of Emission Control and Reduction and Cost Effectiveness for Formaldehyde Model Plant Using a Metal Oxide Catalyst

Emission Source	Control	Total Installed Capital Cost (X 1000)	Annual Operating Cost (X 1000) Fixed Cost	Utilities	Manpower	Recovery Credit	Net	Total VOC Emission Reduction (Mg/yr)	Total VOC Cost Effectiveness (per Mg)
Product absorber vent	Thermal oxidation								
	No heat recovery	$350	$101	$135	$18	$0	$254	142	$1,794
	Steam generation	448	130	135	36	(95)	206	142	1,454
	Recuperative heat	459	133	13	32	0	178	142	1,257
Formaldehyde storage and handling	Vent scrubber	49	14	[a]	3.6	(0.4)	17.2	2.4	7,167

[a] Negligible.

c. **Fugitive Sources** -- A control system for fugitive sources is defined in Appendix C. A separate report[4] covers fugitive emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.

d. **Secondary Sources** -- No control system has been identified for the secondary emissions from the model plant. Secondary emissions and applicable controls are discussed in a separate report.[5]

C. REFERENCES*

1. G. E. Haddeland and G. K. Chang, Report No. 23. Formaldehyde, pp. 104--106, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (Feb. 1967).

2. "Current Prices of Chemicals and Related Materials," Chemical Marketing Reporter 214(5), 34, 35 (July 31, 1978).

3. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

4. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

5. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

VII. SUMMARY

Formaldehyde is produced in the United States from methanol by either a metallic-silver-catalyst process or a metal-oxide-catalyst process. In 1977 the total production from 55 operating plants was 2750 Gg. The formaldehyde production capacity of these plants is reported to be 4066 Gg/yr. With the estimated average annual consumption growth rate of 4 to 5% the production capacity is sufficient to supply the demand through 1982.[1]

Emission sources and control levels for the model plant are summarized in Table VII-1. Projecting these values for the entire domestic formaldehyde industry at full-capacity operation indicates that the total uncontrolled VOC emissions would be 3141 kg/hr. It is estimated that the total VOC emissions from the domestic formaldehyde industry in 1977 were of the order of 1153 kg/hr.

The predominant emission point is the product absorber vent. For the metallic-silver-catalyst process the absorber-vent gas has a high heating value and can be oxidized or be used as supplemental fuel in a steam generator. A VOC reduction efficiency of greater than 99% results when the gas is burned. A thermal oxidation system with a conventional steam-generating heat recovery boiler for the silver catalyst model plant is estimated to cost $540,000. The recovery credit for the steam generated would be $132,000/yr, for a net annual cost of $104,000. The cost effectiveness of the system would be $489 per Mg of VOC removed.

The absorber-vent emissions from a plant using the metal-oxide-catalyst process can also be controlled by thermal oxidation of the gas stream, which would result in a total VOC reduction of greater than 99%. An oxidation system with a conventional steam-generating heat recovery boiler would cost $448,000 for the model plant. The recovery credit for the steam generated would be $95,000 per year. However, since the vent gas contains large amounts of inert components, supplemental fuel must be used to fire the oxidizer. The net annual cost therefore would be $206,000 per year, which results in a cost effectiveness of $1454 per Mg of VOC removed.

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[1] J. L. Blackford, "CEH Marketing Research Report on Formaldehyde," pp. 658.50310--658.5033E in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1977).

Table VII-1. VOC Emission Summary for Model Plant

Emission Source	Stream or Vent Designation (Figs. III-1, -2)	Emission Rate (kg/hr)[a]			
		Metallic-Silver-Catalyst Process		Metal-Oxide-Catalyst Process	
		Uncontrolled	Controlled	Uncontrolled	Controlled
Absorber vent	A	24.5	0.24	16.3	0.16
Fractionator vent	B	8.2	Negligible	NA[b]	NA
Intermittent[c]	C	0.28	0.28	NA	NA
Storage and handling	D,F	0.73	0.075	0.74	0.085
Fugitive	H	5.7	1.09	3.7	0.98
Secondary	K	0.03	0.03	0.2	0.24
Total		39.44	1.71	20.94	1.46

[a] All emissions are based on 8760 hr of operation per year.

[b] Not applicable to process.

[c] Average rate for entire year, based on 8 startups per year.

For those plants using the metal-oxide-catalyst process that do not have a use for the excess steam generated by the heat recovery boiler, an oxidation system with recuperative heat recovery could be installed. This system, by preheating vent gas and combustion air, greatly reduces the supplemental fuel required. This system for the model plant would cost $459,000. Since this system does not produce exportable energy, the net annual cost would be $178,000/yr, for a cost effectiveness of $1257 per Mg of total VOC removed.

The metallic-silver-catalyst process incorporates a fractionator to separate the excess methanol from the product. The emissions from the fractionator vent are controlled in the model plant by recycling the vapor to the process, thus providing essentially 100% VOC control. The cost of the model-plant recycle system is $47,000. With a recovery credit of $11,800 taken for the value of the methanol and formaldehyde that are recovered, the net annual cost is $2700. The cost effectiveness is $35 per Mg of VOC removed.

The model-plant methanol storage emissions are controlled by internal-floating-roof tanks. Costs for internal floating roofs are given in a separate report covering storage and handling.[2] The model-plant formaldehyde-solution storage and handling emissions are controlled by a vent scrubber system. The scrubber cost for either process is $49,000. The net annual cost is $17,200/yr, for a cost effectiveness of $7167 per Mg of VOC removed.

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[2] D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

APPENDIX A

Table A-1. Properties of Anhydrous Formaldehyde and Methanol

	Methanol[a]	Formaldehyde[b]
Synonyms	Methyl alcohol, carbinol, methyl hydroxide	Methanal, methyl aldehyde
Molecular formula	CH_4O	CH_2O
Molecular weight	32.04	30.03
Physical state	Liquid	Colorless gas
Vapor pressure	17.05 kPa at 25°C	259.67 kPa at 25°C
Density	0.7913 at 20°C/4°C	0.815 at 20°C/4°C
Boiling point	64.8°C	-21°C
Melting point	-93.9°C	-92°C
Water solubility	Infinite	Soluble

[a] From: J. Dorigan *et al*, "Formaldehyde," p. AIII-154 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N)*, Rev 1, Appendix III, MTR-7248, MITRE Corp., McLean, VA (September 1976).

[b] *Ibid.*, p AIII-12.

Table A-2. Properties of Formaldehyde Solution (37 wt %)

Synonyms	Formalin
Molecular formula	CH_2O
Molecular weight	30.03
Physical state	Clear liquid
Density	1.113 g/ml at 18°C
Boiling point	99°C
Water solubility	Soluble

Table A-3. Properties of Paraformaldehyde

Molecular formula	$HO(CH_2O)_{\underline{n}}H$[a]
Molecular weight	$(30.03)_{\underline{n}} + 18$[a]
Physical state	White solid
Vapor specific gravity	0.815 at 20°C/4°C
Boiling point	Depolymerizes at 120 to 200°C
Melting point	120 to 170°C
Water solubility	Soluble

[a] n ranges from about 8 to 100.

APPENDIX B

Table B-1. Air-Dispersion Parameters for Metallic-Silver-Catalyst Process Model Plant with a Capacity of 45 Gg/yr

Source	Total Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled Emissions			
Absorber vent	6.80	19.8	0.61	302	3.18	3.32
Fractionator vent	2.27		0.05	297	0.02	2.00
Startup vent[a]	167.20	21.3	0.51	533	5.59	8.37
Methanol recycle tank	0.01	2.4	1.4	297		
Methanol storage (2 tanks)	0.11	7.3	5.8	Ambient		
Formaldehyde storage (4 tanks)	0.05	7.3	5.8	327		
Formaldehyde handling	0.03			327		
Fugitive emissions[b]	1.58			Ambient		
Secondary emissions	0.01	c	c	Ambient		
			Controlled Emissions			
Absorber vent[d]	0.068	30.0	0.61	533	9.60	10
Methanol storage (2 tanks)	0.017	7.3	5.8	Ambient		
Formaldehyde storage and handling (4 tanks)	0.003	7.3	5.8	302		
Fugitive emissions	1307			Ambient		

[a] Peak flow conditions during startup.

[b] Fugitive emissions are distributed over a 50-m by 150-m area.

[c] Surface of ground level waste water treatment system.

[d] Thermal oxidizer system.

Table B-2. Air-Dispersion Parameters for Metal-Oxide-Catalyst Process Model Plant with a Capacity of 45 Gg/yr

Source	Total VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled Emissions			
Absorber vent	4.54	19.8	0.76	302	4.99	3.34
Methanol storage (2 tanks)	0.12	7.3	5.8	Ambient		
Formaldehyde storage (4 tanks)	0.05	7.3	5.8	327		
Formaldehyde handling	0.03			327		
Fugitive emissions[a]	1.06			Ambient		
Secondary emissions	0.07			Ambient		
			Controlled Emissions			
Absorber vent[b]	0.045	30.0	0.76	533	14.60	10
Methanol storage[c] (2 tanks)	0.019	7.3	5.8	Ambient		
Formaldehyde storage and handling[d] (4 tanks)	0.003	7.3	5.8	302		
Fugitive emissions[e]	0.288			Ambient		

[a] Fugitive emissions are distibuted over a 50-m by 150-m area.

[b] Thermal oxidizer system.

[c] Internal-floating-roof tanks.

[d] Vent scrubber.

[e] Repaired and maintained.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST ESTIMATE DETAILS

This appendix contains sample calculations showing how the costs presented in this report were estimated.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure D-1 illustrates this relationship. The contingency allowance indicated is included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. D-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternative within the limits of accuracy indicated.

A. THERMAL OXIDIZER——METALLIC-SILVER-CATALYST MODEL PLANT

To determine the cost estimate for controlling the vent emissions from the silver catalyst model-plant absorber vent, the emission flow details were taken from Table IV-3:

$$628 \text{ g/kg} \times 45 \text{ Gg/yr} \div 8760 \text{ hr/yr} \times 2.205 \text{ lb/kg} = 7114 \text{ lb/hr}.$$

The flow in mole/hr was calculated for each component; the total flow was calculated to be 310 lb-moles/hr, or 1855 scfm. The total lower heating value was calculated to be 8.55 MM Btu/hr, or 77 Btu/scf.

The following control costs and cost-effective estimates given in Table D-1 were developed by making semilog extrapolations of the tables on pages B-22 and B-23 of the control device evaluation report for thermal oxidation.[1]

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[1] J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

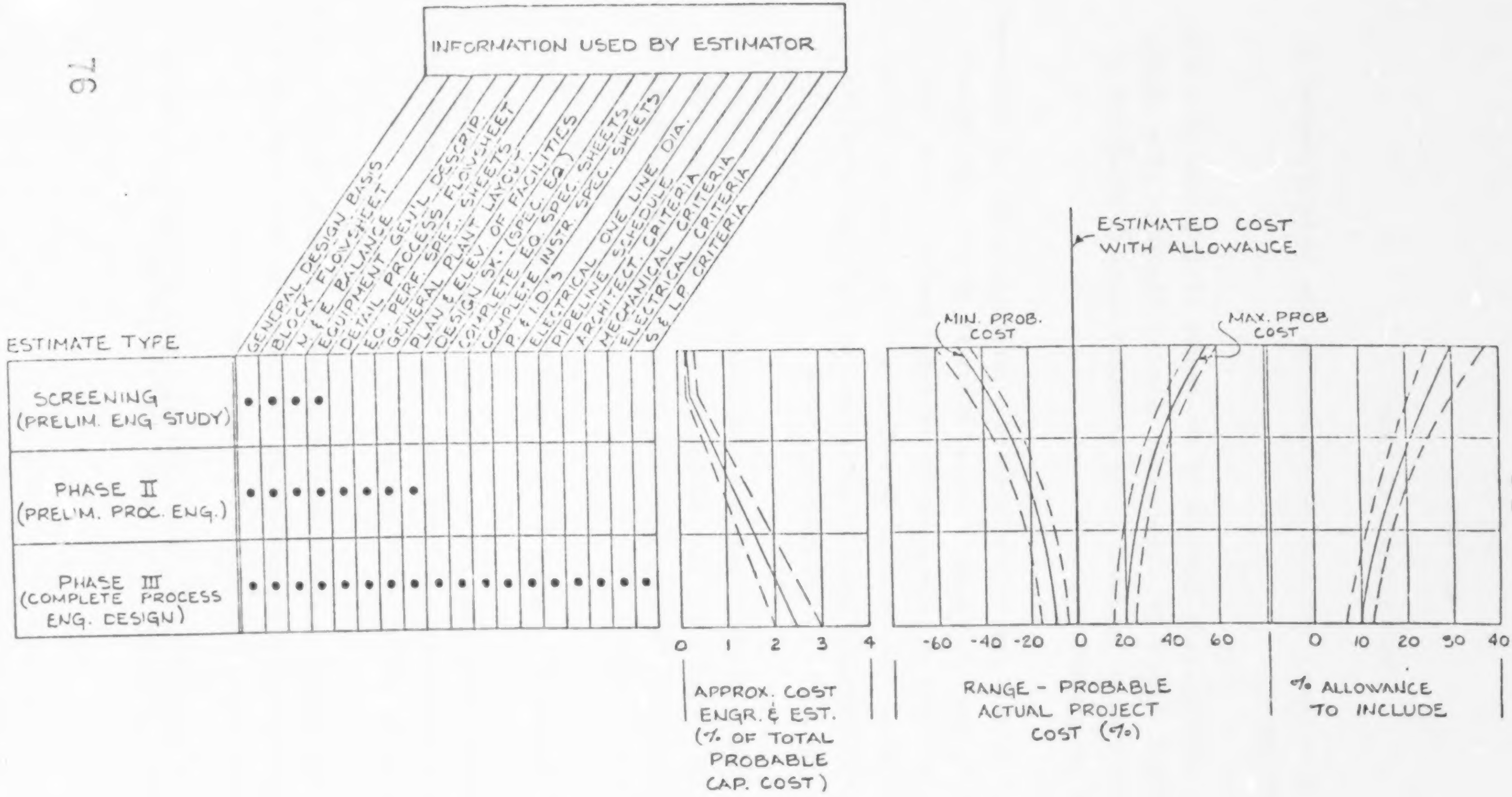

Fig. D-1. Precision of Capital Cost Estimates

Table D-1.

Plant Size (Gg)	Rate (scfm)	Installed Capital Cost	Annual Cost (X1000) Fixed Cost	Utilities	Manpower	Recovery Credit	Net	Operating Cost (per scfm)	VOC Reduction (Mg/yr)	Cost Effectiveness (per Mg)
					No Heat Recovery					
23	927	$327	$ 95	$ 21	$18	$0	$134	$144	106	$1,262
45	1855	370	107	43	18	0	168	90	212	791
113	4637	430	125	105	18	0	248	53	531	467
					With 250-psi Steam Generator					
23	927	$438	$127	$21	$36	$66	$118	$127	106	$1,111
45	1855	540	157	43	36	132	104	56	212	489
113	4637	675	196	105	36	329	7	1.5	531	13.2

B. THERMAL OXIDIZER—METAL-OXIDE-CATALYST MODEL PLANT

The emission flow details were taken from Table IV-5. Since the oxygen content is significant and the thermal oxidation control device evaluation report[1] is based on no oxygen in the feed, the oxygen and the corresponding nitrogen will be subtracted and assumed to be part of the air added for combustion.

The listed emissions of 1178 g/kg are therefore reduced by 93.2 g of oxygen and 93.2 (77/23) = 312 g of nitrogen. With zero oxygen and 1014 - 312 = 702 g of nitrogen the total emissions for sizing the thermal oxidizers are 773 g/kg of formaldehyde solution:

773 g/kg X 45 Gg/8760 X 2.205 lb/kg = 8756 lb/hr.

Component	Feed Rate (lb/hr)	Heat Capacity		For Thermal Oxidizer Design (lb mole/hr)
		(Btu/lb)	(Btu/hr)	
Formaldehyde	5.3	7,410	39,273	0.17
Methanol	21.3	8,896	189,484	0.67
Dimethyl ether	9.3	12,358	114,929	0.21
CO	168.1	4,347	730,731	6.00
Totals	204	5,267	1,074,417	7.05
Nitrogen with equivalent air subtracted				284.03
Oxygen	0			0
CO_2	25.4			0.58
				291.66 X 359 = 104,706 scf/hr = 1745 scfm

Therefore 1,074,417 ÷ 104,706 = 10.26 Btu/scf.

The control costs and cost-effectiveness estimates given in Table D-2 were developed by making a semilog extrapolation of the tables on page B-16 of the control device evaluation report for thermal oxidation.[1]

Table D-2.

Plant Size (Gg)	Rate (scfm)	Installed Capital Cost	Annual Cost (X 1000)					Operating Cost (per scfm)	VOC Reduction (Mg/yr)	Cost Effectiveness (per Mg)
			Fixed Cost	Utilities	Manpower	Recovery Credit	Net Annual Cost			
					No Heat Recovery					
23	872	$300	$87	$67	$18		$172	$192	71	$2429
45	1745	350	101	135	18		254	145	142	1794
113	4362	415	120	338	18		476	109	354	1344
					70% Recuperative Heat Recovery					
23	872	$370	$107	$ 6	$32		$145	$166	71	$2048
45	1745	459	133	13	32		178	102	142	1257
113	4362	575	167	32	32		231	53	354	652
					250-psia Steam Generation					
23	872	$360	$140	$ 67	$36	$47	$160	$183	71	$2260
45	1745	448	130	135	36	95	206	118	142	1454
113	4362	563	164	339	36	237	302	69	354	853

C. FRACTIONATOR—JET CONDENSER SYSTEM——METALLIC-SILVER-CATALYST PROCESS

The standard 56-ft^2 jet condenser is adequate for the model plant. The capital cost for the installed condenser with valving, fitting, piping, gauges, liquid separator, level control, and pump is estimated to be $47,000.

Plant Size (Gg)	VOC Reduction (Mg/yr)	Installed Capital Cost	Annual Cost (X 1000)					Cost Effectiveness (per Mg)
			Fixed Cost	Cooling Water	Manpower	Recovery Credit	Net	
23	35.2	$47	$14	$0.5	Negligible	$6.0	$ 8.5	$241
45	71.5	47	14	0.5	Negligible	11.8	2.7	35
113	173.1	49	14	0.7	Negligible	29.8	(15.4)	(89)

D. FRACTIONATOR VENT EMISSIONS SCRUBBER—METALLIC-SILVER-CATALYST PROCESS

The scrubber for the fractionator for the model plant is designed to handle 20 gpm of water and a gas flow of 10 scfm. The scrubber for the model plant is made of type 304 stainless steel and is 8 in. in diameter and 10 ft high, with 8 ft of porcelain rings. There is no significant cost for utilities because the water will also be used as feedwater for the product absorber.

Plant Size (Gg)	VOC Reduction (Mg/yr)	Installed Capital Cost	Annual Cost (X 1000)				Cost Effectiveness (per Mg)
			Fixed Cost	Manpower	Recovery Credit	Net	
23	34.7	$38	$11	$3.6	$5.9	$ 8.7	$251
45	67.9	40	12	3.6	11.7	3.9	57
113	170.5	52	15	3.6	29.3	(10.7)	(63)

E. FORMALDEHYDE STORAGE SCRUBBER

All of the scrubber system for formaldehyde storage emissions is made of type 304 stainless steel. The scrubber for the model plant is 8 in. in diameter and 10 ft high, with 8 ft of porcelain rings. There is no significant cost for utilities.

Plant Size (Gg)	VOC Reduction (Mg/yr)	Installed Capital Cost	Annual Cost (X 1000)				Cost Effectiveness (per Mg)
			Fixed Cost	Manpower	Recovery Credit	Net	
23	1.2	$46	$13	$3.6	$0.2	$16.4	$13,667
45	2.4	49	14	3.6	0.4	17.2	7,167
113	5.0	61	18	3.6	1.1	20.5	3,417

APPENDIX E

EXISTING PLANT CONSIDERATIONS

Table E-1 lists process emission control devices reported to be in use by industry. To gather information for the preparation of this report, two site visits were made to manufacturers of formaldehyde. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Research Triangle Park, NC.[1,2] Some of the pertinent information concerning process emissions from these existing formaldehyde plants is presented in this appendix. Pertinent process emission information was also obtained from the Chemical Manufacturers Association and from a number of formaldehyde producers who submitted comments in response to the draft of this report issued in February 1979.

A. PROCESS EMISSIONS FROM EXISTING PLANTS

1. Celanese, Bishop, TX[1]

The formaldehyde production facility consists of four metallic-silver-catalyst process units. The process emissions are controlled by two incinerators. Heat is recovered from the incinerator flue gases. The following composition is reported to be typical for the process vent emissions:

Component	Amount (%)
Hydrogen	20.57
Nitrogen + air	74.03
Methane	0.02
Methylal	0.19
Methyl formate	0.62
Methanol	0.06
Carbon monoxide	0.64
Carbon dioxide	3.87

Celanese has been averaging 1 or 2 startups a year per unit, and vents the absorber emissions to the atmosphere during startup.

2. Borden, Fayetteville, NC[2]

The formaldehyde production facility consists of three independent silver catalyzed processes. The emissions from the product absorber consist of nitrogen, hydrogen, carbon dioxide, carbon monoxide, and oxygen, along with small quantities of VOC consisting of methyl formate, methylal, and methanol. Absorber vent emissions are controlled by burning the gas in specially designed steam generators. The system was developed by Borden and its design is proprietary. The plant does not operate unless a boiler is in operation. During startup of a formaldehyde unit the absorber vent gases are emitted to the atmosphere until stable operation is achieved. These are normally from 4 to 12 startups per year. Startup venting to the atmosphere lasts from 1 to 2 hr.

The fractionator vacuum system emission is discharged to the atmosphere. No data were available on the composition or flow from the vent.

3. Monsanto Plastics & Resins Co.[3]

Monsanto objects to any consideration of the use of a flare during startup because of the wide change in relative compositions of H_2 and O_2. They emphasize the point that emissions are reduced by operating at one-half rate until the startup procedure is completed.

Monsanto states that with their design of a vent condenser using refrigerated water at 35°F to condense emissions from the product fractionator, they estimate VOC emissions to be reduced by 80%. Methanol is thereby recovered in the finished product, thus eliminating a subsequent waste disposal step.

4. Georgia-Pacific Corporation[4]

Georgia-Pacific states that new test data indicate that the emissions from the absorber for their Lufkin metal-oxide-catalyst plant are much greater than they had estimated for their permit application and much higher than indicated for the metal oxide model plant in this report. The averages of five absorber emission test results are reported as follows:

	Methanol Feed (wt %)
Dimethyl ether	1.81
Methanol	0.31
Formaldehyde	0.02
Total VOC	2.14

5. Reichhold Chemicals, Inc.[5]

Test data for the Reichhold Moncure metal-oxide plant indicate that their absorber vent emissions are considerably less than the emissions listed for the metal oxide model plant in this report. The averages of three absorber emission test results are reported as follows:

	Amount (ppm)	Formaldehyde Produced (g/kg)
Formaldehyde	171	0.0037
Methanol	3380	0.0782
Dimethyl ether	1847	0.0614
Total VOC	5398	0.1433

B. TOTAL INDUSTRY EMISSIONS

Emissions from industry were estimated based on actual emission rates reported by the individual plants. When the data reported were incomplete, the emission rates used for the control measures reported by the plants (see Table E-1) were based on model-plant data. For those plants not reporting data it was assumed that control measures similar to those indicated in Table E-1 would exist for other plants operated by the same company. It was estimated that secondary emissions were uncontrolled for all plants and that maintenance programs for the control of fugitive emissions averaged half way between controlled and uncontrolled.

Based on the above, total emissions from all plants during 1977 were approximately 10 Gg. The emissions from these plants would have been approximately 18 Gg during 1977 if the emissions had been uncontrolled, or 1 Gg if all plants had been controlled by the measures described for the model plants. It appears, then, that the current level of control obtained by the industry is approximately 57% of that possible from application of model-plant controls.

Table E-1. Control Devices Currently Used by the Domestic Formaldehyde Industry[a]

Company and Location	Type of Process	Control Device		
		For Absorber Vent	For Fractionator Vent[b]	For Storage Tank Vents
Allied				
Irontown, OH	Silver catalyst	Thermal oxidizer (100%)[c]	D	None
Borden				
Fayetteville, NC	Silver catalyst	Steam boiler (100%)[c]	NR	Conservation vent
Geismar, LA	Silver catalyst	Steam boiler	NR	None
Springfield, OR	Silver catalyst	Steam boiler (100%)[c]	D	Conservation vent
Celanese				
Bishop, TX	Silver catalyst	Thermal oxidizer (100%)[c]	NR	None
Newark, NJ	Metal oxide	Demister	NA	NR
Du Pont				
Belle, WV	Silver catalyst	Thermal oxidizer (99.8%)[c]	NR	None
Healing Spring, NC	Silver catalyst	Thermal oxidizer	NR	Vent condenser
Lufkin, TX	Metal oxide	None	NA	NR
LaPorte, TX	Silver catalyst	Flare	NR	Vent condenser
GAF				
Calvert City, KY	Metal oxide	Demister	NA	None
Georgia-Pacific				
Columbus, OH	Metal oxide	Demister	NA	None
Crossett, AR	Silver catalyst	None	None	None
Vienna, GA	Silver catalyst	Demister	D	None
Gulf				
Vicksburg, MS	Metal oxide	None	NA	Conservation vent
Hercules				
Wilmington, NC	Silver catalyst	None	None	None
Hooker				
North Tonawanda, NY	Silver catalyst	Steam boiler	D	None
Monsanto				
Addyston, OH	Silver catalyst	Refrigerated condenser (96.1%)[c]	NR	NR
Chocolet Bayou, TX	Silver catalyst	None	Condenser	None
Reichhold				
Houston, TX	Metal oxide	None	NA	Conservation vent
Kansas City, KA	Silver catalyst	None	Condenser	None
Moncure, NC	Metal oxide	None	NA	Conservation vent
Tuscaloosa, AL	Silver catalyst	Demister	D	None
Tenneco				
Fords, NJ	Metal oxide	Scrubber (94%)[c]	NA	Scrubber
Garfield, NJ	Silver catalyst	None	Scrubber	None

[a] For those plants reporting information; see refs. 1—5.

[b] D - distillation column used rather than vacuum fractionation.
NR - not reported.
NA - not applicable to metal-oxide-catalyst process.

[c] Reported efficiency for control device on absorber vent.

C. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

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3. N. B. Galluzzo, Monsanto Resins Co., letter dated July 13, 1979, to R. J. Lovell, IT Enviroscience.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX F

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C. A. Williams, *EPA Questionnaire for Reichhold Chemicals, Inc.*, Kansas City Plant, Aug. 7, 1972.

REPORT 2

Methanol

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This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

D43P

89

CONTENTS OF REPORT 2

Page

I. ABBREVIATIONS AND CONVERSION FACTORS I-1

II. INDUSTRY DESCRIPTION II-1
  A. Reason for Selection II-1
  B. Usage and Growth II-1
  C. Domestic Producers II-3
  D. References II-7

III. PROCESS DESCRIPTION III-1
  A. Introduction III-1
  B. Low-Pressure Process III-1
  C. Process Variations III-5
  D. References III-7

IV. EMISSIONS IV-1
  A. Low-Pressure Process IV-1
  B. Process Variations IV-8
  C. References IV-9

V. APPLICABLE CONTROL SYSTEMS V-1
  A. Low-Pressure Process V-1
  B. Process Variations V-4
  C. References V-5

VI. IMPACT ANALYSIS VI-1
  A. Environmental and Energy Impacts VI-1
  B. Control Cost Impact VI-3
  C. References VI-4

VII. SUMMARY VII-1

APPENDICES OF REPORT 2

		Page
A.	PHYSICAL PROPERTIES OF METHANOL, DIMETHYL ETHER, AND METHYL FORMATE	A-1
B.	AIR-DISPERSION PARAMETERS FOR MODEL PLANT	B-1
C.	FUGITIVE-EMISSION FACTORS	C-1
D.	EXISTING PLANT CONSIDERATIONS	D-1

TABLES OF REPORT 2

Number		Page
II-1	Methanol Usage and Growth	II-2
II-2	Methanol Capacity	II-4
IV-1	Total Uncontrolled VOC Emissions for Methanol Model Plant	IV-3
IV-2	Estimated Composition of Purge Gas from Model Plant	IV-4
IV-3	Composition of Distillation Vent Gas from Model Plant	IV-5
IV-4	Storage Tank Data for Methanol Model Plant	IV-6
V-1	VOC Controlled Emissions for Methanol Model Plant	V-2
VI-1	Environmental Impact of Controlled Methanol Plant	VI-2
VII-1	Emission Summary for Methanol Model Plant	VII-2
A-1	Physical Properties of Methanol	A-1
A-2	Physical Properties of Dimethyl Ether	A-2
A-3	Physical Properties of Methyl Formate	A-3
B-1	Air-Dispersion Parameters for Model Plant	B-1
D-1	Emission Control Devices or Techniques Currently Used	D-3

FIGURES OF REPORT 2

II-1	Locations of Plants Manufacturing Methanol	II-5
III-1	Flow Diagram for Uncontrolled Model Plant for Production of Methanol	III-4

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

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CONTENTS

		Page
	INTRODUCTION	vii
	Product Report	Page
1.	FORMALDEHYDE	1-i
2.	METHANOL	2-i
3.	ETHYLENE	3-i
4.	ETHYLENE OXIDE	4-i
5.	VINYL ACETATE	5-i
6.	ACETALDEHYDE	6-i
7.	ETHANOLAMINES	7-i
8.	ETHYLENE GLYCOL	8-i
9.	GLYCOL ETHERS	9-i

INTRODUCTION

A. SOCMI PROGRAM

Concern over widespread violation of the national ambient air quality standard for ozone (formerly photochemical oxidants) and over the presence of a number of toxic and potentially toxic chemicals in the atmosphere led the Environmental Protection Agency to initiate standards development programs for the control of volatile organic compound (VOC) emissions. The program goals were to reduce emissions through three mechanisms: (1) publication of Control Techniques Guidelines to be used by state and local air pollution control agencies in developing and revising regulations for existing sources; (2) promulgation of New Source Performance Standards according to Section 111(b) of the Clean Air Act; and (3) promulgation, as appropriate, of National Emission Standards for Hazardous Air Pollutants under Section 112 of the Clean Air Act. Most of the effort was to center on the development of New Source Performance Standards.

One program in particular focused on the synthetic organic chemical manufacturing industry (SOCMI), that is, the industry consisting of those facilities primarily producing basic and intermediate organics from petroleum feedstock meterials. The potentially broad program scope was reduced by concentrating on the production of the nearly 400 higher volume, higher volatility chemicals estimated to account for a great majority of overall industry emissions. EPA anticipated developing generic regulations, applicable across chemical and process lines, since it would be practically impossible to develop separate regulations for 400 chemicals within a reasonable time frame.

To handle the considerable task of gathering, assembling, and analyzing data to support standards for this diverse and complex industry, EPA solicited the technical assistance of IT Enviroscience, Inc., of Knoxville, Tennessee (EPA Contract No. 68-02-2577). IT Enviroscience was asked to investigate emissions and emission controls for a wide range of important organic chemicals. Their efforts focused on the four major chemical plant emission areas: process vents, storage tanks, fugitive sources, and secondary sources (i.e., liquid, solid, and aqueous waste treatment facilities that can emit VOC).

B. REPORTS

To develop reasonable support for regulations, IT Enviroscience gathered data on about 150 major chemicals and studied in-depth the manufacture of about 40 chemical products and product families. These chemicals were chosen considering their total VOC emissions from production, the potential toxicity of emissions, and to encompass the significant unit processes and operations used by the industry. From the in-depth studies and related investigations, IT Enviroscience prepared 53 individual reports that were assembled into 10 volumes. These ten volumes are listed below:

Volume 1 : Study Summary
Volume 2 : Process Sources
Volume 3 : Storage, Fugitive, and Secondary Sources
Volume 4 : Combustion Control Devices
Volume 5 : Adsorption, Condensation, and Absorption Devices
Volume 6-10: Selected Processes

This volume is a compilation of individual reports for the following chemical products: formaldehyde, methanol, ethylene, ethylene oxide, vinyl acetate, acetaldehyde, ethanolamines, ethylene glycol, and glycol ethers. The reports generally describe processes used to make the products, VOC emissions from the processes, available emission controls, and the costs and impacts of those controls (except that abbreviated reports do not contain control costs and impacts). Information is included on all four emission areas; however, the emphasis is on process vents. Storage tanks, fugitive sources, and secondary sources are covered in greater detail in Volume III. The focus of the reports is on control of new sources rather than on existing sources in keeping with the main program objective of developing new source performance standards for the industry. The reports do not outline regulations and are not intended for that purpose, but they do provide a data base for regulation development by EPA.

C. MODEL PLANTS

To facilitate emission control analyses, the reports introduce the concept of a "model plant" (not in abbreviated reports). A model plant by definition is a representation of a typical modern process for production of a particular chemical. Because of multiple production routes or wide ranges in typical production capacities, several model plants may be presented in one product report. The model plants can be used to predict emission characteristics of a new plant. Of course, describing exactly what a new plant will be like is difficult because variations of established production routes are often practiced by individual companies. Nonetheless, model plants provide bases for making new-plant emission estimates (uncontrolled and controlled), for selecting and sizing controls for new plants, and for estimating cost and environmental impacts. It is stressed that model-plant analyses are geared to new plants and therefore do not necessarily reflect existing plant situations.

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Methanol was selected for consideration because it is produced in large amounts and has a moderate volatility (see Appendix A for pertinent physical properties), both of which contribute to potentially high emissions of volatile organic compounds (VOC).

B. USAGE AND GROWTH

The end uses of methanol and the expected growth rate for each use are given in Table II-1.* Formaldehyde production is the largest consumer (~40%) of methanol and is expected to continue to be through 1981, when it will still account for 37% to 38% of the domestic consumption. The fastest growing use of methanol is in the production of acetic acid, which by 1981 will account for 9 to 10% of the domestic consumption and will make it the second-largest consumer of methanol. Methanol is also used as a solvent, to a small extent as a fuel, and in the production of numerous chemicals; only the largest consumers are shown in Table II-1. Fuel use has been as an injection fluid in certain aircraft engines and as automotive fuel in racing cars and boats. A new fuel use is in the production of methyl tertiary butyl ether (MTBE), approved by the EPA in 1979 as a high-octane component in gasoline. By 1983 this use could equal or exceed the use of methanol to produce acetic acid.[1,2]

The domestic methanol production capacity for 1980 is reported to be about 4,310,000 Mg/yr[2] and does not include a plant that has been mothballed by Du Pont[3] or a Valley Nitrogen plant that has been on stand-by since 1977. Two new producers (Arco Chemical and Getty Refining and Marketing) are planning new methanol capacities by 1983 in addition to expansions by existing producers, and so there should be sufficient capacity to supply 1983 domestic demand if it grows at the projected rate of 7% per year. Some methanol will be imported to help meet the demand in times of shortages.[2]

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*In order to minimize the revision time, the 1976 data that were used for the original draft of this report are retained. For our purposes the differences are not believed to be significant.

Table II-1. Methanol Usage and Growth*

End Use	Consumption For 1976 (%)	Average Growth For 1976—1981 (%/yr)
Formaldehyde	42	5
Solvents	8	7
Chloromethanes	8	7
Acetic acid	5	24
Methylamines	5	8
Methyl methacrylate	5	7
Dimethyl terephthalate	4	6
Glycol methyl ethers	1	4
Inhibitor for formaldehyde	1	3
Miscellaneous and fuel uses	21	8

*See ref 1.

C. DOMESTIC PRODUCERS

There were 8 producers operating 10 methanol plants in the United States in 1980. Table II-2 lists the producers, locations, and capacities;[2] Fig. II-1 shows the plant locations.

Producing Companies

1. Air Products

About 45% of the methanol capacity is required to operate the methylamines facilities at capacity.[1]

2. Borden

Acetic acid and formaldehyde are produced from methanol at Geismar, LA, and formaldehyde is produced at several other locations. The total estimated requirement for methanol is about 70% of capacity.[1] Borden has announced that the methanol plant will be modernized and expanded in 1980, with the existing high-pressure process being replaced by ICI low-pressure synthesis technology.[2]

3. Celanese

Formaldehyde production and acetic acid production require about 45% of the total methanol capacity of two plants.[1]

4. Du Pont

Formaldehyde, dimethyl terephthalate, methyl amines, and methyl methacrylate are produced at several locations and consume about 75% of the methanol capacity of the Beaumont, TX, plant. A new 600,000-Mg/yr methanol plant has been started up at Deer Park, TX,[1,2] and a 350,000-Mg/yr plant at Orange, TX, has been mothballed.[3]

5. Georgia-Pacific

Formaldehyde is produced from methanol at several locations and at capacity requires about half of the methanol produced by their methanol plant when it is run at capacity.[1]

Table II-2. Methanol Capacity[a]

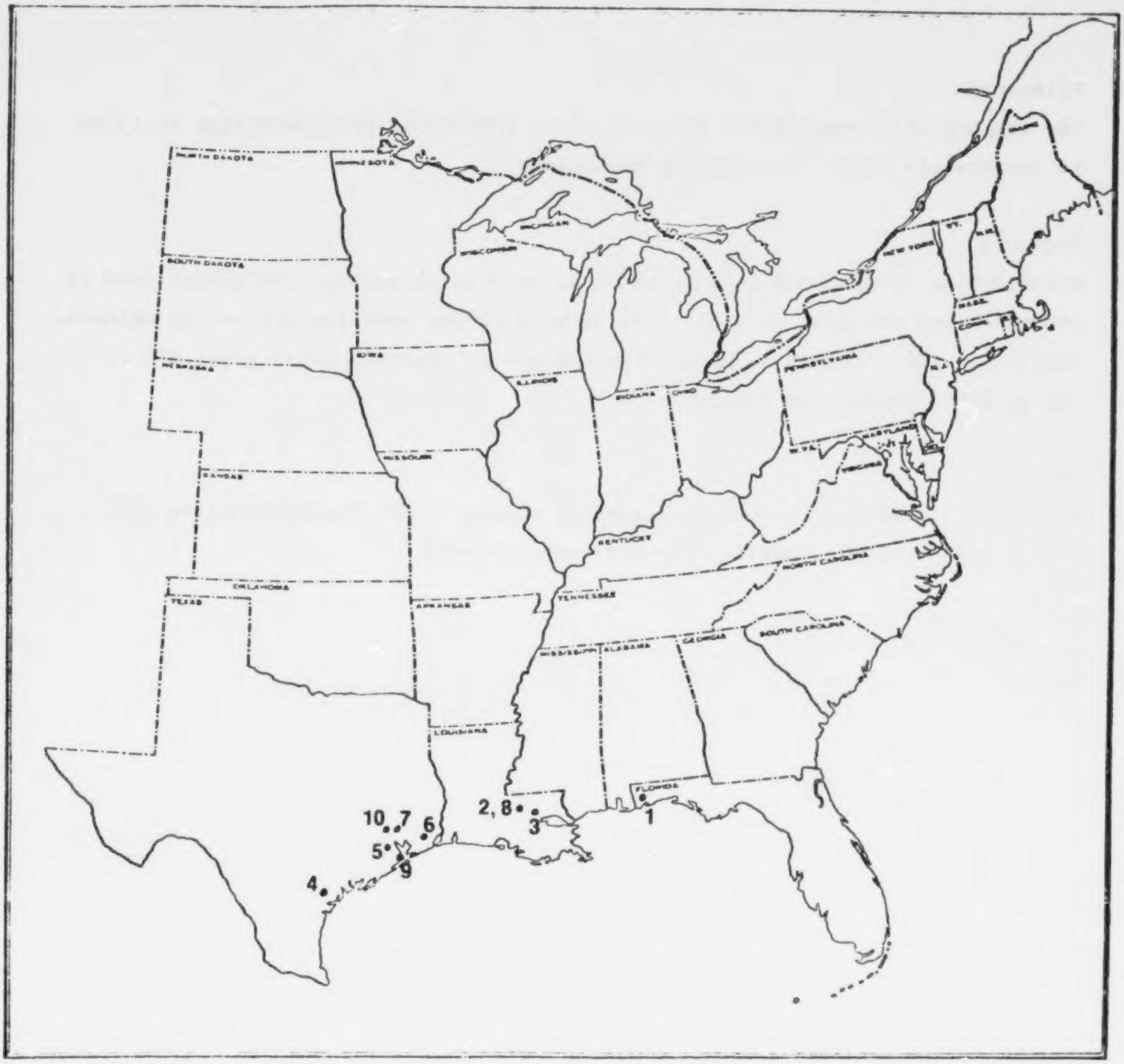
Plant	Capacity as of 1980 (Mg/yr)	Process Used
Air Products, Pensacola, FL	150,000	High pressure
Allemania, Plaquemine, LA	300,000	High pressure[b]
Borden, Geismar, LA	540,000	Low pressure[c]
Celanese, Bishop, TX	450,000	Low pressure
Celanese, Clear Lake, TX	690,000	Low pressure
Du Pont, Beaumont, TX	680,000	High pressure
Du Pont, Deer Park, TX	600,000	Low pressure
Georgia-Pacific, Plaquemine, LA	360,000	Low pressure
Monsanto, Texas City, TX	300,000	Low pressure
Tenneco, Houston, TX	240,000	High pressure[d]
Total	4,310,000	

[a] See ref 2.

[b] Allemania will rebuild in 1981 the existing plant (formerly Hecofina) to incorporate Lurgi low-pressure process with expanded capacity of 360,000 Mg/yr.

[c] Borden is to replace its existing high-pressure process with ICI low-pressure technology by the end of 1980.

[d] Tenneco will convert its plant in 1981 to Lurgi low-pressure process with a capacity of 390,000 Mg/yr.



1. Air Products, Pensacola, FL
2. Allemania, Plaquemine, LA
3. Borden, Geismar, LA
4. Celanese, Bishop, TX
5. Celanese, Clear Lake, TX
6. Du Pont, Beaumont, TX
7. Du Pont, Deer Park, TX
8. Georgia-Pacific, Plaquemine, LA
9. Monsanto, Texas City, TX
10. Tenneco, Houston, TX

Fig. II-1. Locations of Plants Manufacturing Methanol

6. Allemania

The company will rebuild the existing plant (purchased from Hercofine in 1979) to incorporate Lurgi low-pressure technology.[2]

7. Monsanto

Formaldehyde is produced from methanol at several locations, and acetic acid is produced from methanol in a facility located in the same complex as the methanol facility. The combined methanol requirements at capacity total about 80% of the methanol production capacity.[1]

8. Tenneco

Operation at capacity of two formaldehyde plants in New Jersey requires only 20% of the methanol capacity; the remainder is sold.[1]

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Almost all methanol produced in the United States is made from natural gas. The natural gas is steam reformed to produce synthesis gas, consisting of a mixture of carbon monoxide, carbon dioxide, and hydrogen, which is then converted into methanol. The large new methanol plant started up in 1980 by Du Pont at Deer Park, TX, is supplied with synthesis gas produced by partial oxidation of residual fuel oil. The off-gases from the partial oxidation of natural gas for acetylene manufacture contain the right proportions of carbon monoxide, carbon dioxide, and hydrogen for methanol synthesis and have been used for the production of methanol. Other potential sources of synthesis gas are coal gasification, pyrolysis of garbage, timber wastes, agricultural wastes, or municipal solid wastes, and even a steel plant's basic oxygen furnace off-gases. None of these sources are economically feasible at this time.[1—3]

The synthesis gas is converted to methanol by either a high-pressure (28 to 45 MPa) process or by one of the more recently developed low-pressure (5 to 10 MPa) processes. All new methanol capacity is based on low-pressure technology. Although processes have been developed that employ medium pressures of 15 to 18 MPa, none are used in the United States.[1—5]

A small smount of methanol is obtained as a by-product from the oxidation of butane to produce acetic acid and from destructive distillation of wood to produce charcoal. When wood is carbonized by prolonged heating, condensable and noncondensable volatiles are given off. The condensable portion - called pyroligneous acid - contains methanol, acetic acid, and tars. Natural methanol and acetic acid can be recovered by refining the pyroligeneous acid after the tars have been removed. This process was discontinued in the United States during the early 1970s. Methanol is regenerated in the production of polyester from dimethyl terephthalate and is usually recycled to produce additional dimethyl terephthalate.[1]

B. LOW-PRESSURE PROCESS

The steam reforming of natural gas (methane) to produce synthesis gas takes place according to the following reactions:

$$\underset{\text{(methane)}}{CH_4} + \underset{\text{(steam)}}{H_2O} \longrightarrow \underset{\text{(hydrogen)}}{3\,H_2} + \underset{\text{(carbon monoxide)}}{CO}$$

$$\underset{\text{(methane)}}{CH_4} + \underset{\text{(steam)}}{2H_2O} \longrightarrow \underset{\text{(hydrogen)}}{4H_2} + \underset{\text{(carbon dioxide)}}{CO_2}$$

The tubular reformer operates at 800 to 850°C and 1.7 to 2.1 MPa and is heated with fuel gas as both reactions are endothermic. A promoted nickel-based catalyst is used and the steam to methane ratio is controlled to give a synthesis gas that contains, in addition to the hydrogen and carbon oxides, only small amounts of unreacted methane, plus the nitrogen and argon that were fed with the natural gas.[3—6]

The hydrogen and carbon oxides in the synthesis gas are converted to methanol by the exothermic reactions:

$$\underset{\text{(hydrogen)}}{2H_2} + \underset{\text{(carbon monoxide)}}{CO} \longrightarrow \underset{\text{(methanol)}}{CH_3OH}$$

$$\underset{\text{(hydrogen)}}{3H_2} + \underset{\text{(carbon dioxide)}}{CO_2} \longrightarrow \underset{\text{(methanol)}}{CH_3OH} + \underset{\text{(water)}}{H_2O}$$

The reaction conditions are a temperature of 200 to 300°C and a pressure of 5 to 10 MPa. A very active copper-based synthesis catalyst is used that is easily poisoned by sulfur compounds. The synthesis gas feed preferably contains less than 1.0 ppm of sulfur, and if possible less than 0.1 ppm. When produced by steam reforming of natural gas the synthesis gas contains an excess of hydrogen over the stoichiometric amount needed; so carbon dioxide may be added to the reformer feed or to the synthesis gas to provide the proper proportions.[1,3—10]

Efficient waste heat recovery from the reformer flue gases, from the synthesis gas leaving the reformer, and from the product gases leaving the converter and the use of purge gases and waste liquids as either fuel or as feeds to other processes are very important factors affecting operating costs. Optimization by a systems approach to the design of the operating parameters of all the sections of the methanol plant—reforming, compression, synthesis, distillation, and heat recovery—reduces energy requirements.[2] The overall plant may be self-supporting with regard to steam during normal operation.[9]

Figure III-1 is a typical flow diagram for a low-pressure methanol process. Natural gas (Stream 1) is desulfurized, generally by adsorption on activated carbon, and then fed with steam and carbon dioxide (Streams 2 and 3) to a tubular reformer fired with fuel gas. Heat is recovered from the synthesis gas leaving the reformer (Stream 4) by producing steam in a heat recovery system. The cooled synthesis gas (Stream 5) is compressed by the makeup gas compressor and added to recycled synthesis gas (Stream 6) in the synthesis loop. The combined synthesis gas is preheated to the reaction temperature by heat exchange with the product gas (Stream 7) leaving the converter; the preheated gas (Stream 8) then enters the converter. A portion of the cold gas (Stream 9) from the synthesis loop is injected into the converter at several locations to control the reaction temperature. The product gas leaving the converter (Stream 7) is cooled by heat exchange with the synthesis gas (Stream 6) and then further cooled by the heat recovery and condensing system to condense methanol. The unreacted synthesis gas and condensed methanol (Stream 10) go to the separator, where the crude methanol (Stream 11) is removed from the unreacted gas and sent to the flash tank. The synthesis gas from the separator is compressed by the recirculating compressor for recycle after a portion has been purged (Stream 12) to remove inert gases (Vent A) from the system. The pressure on the crude methanol is reduced to near-atmospheric in the flash tank, where dissolved gases flash off (Stream 13) and leave with the purge gas (Vent A). The degassed crude methanol from the flash tank (Stream 14) goes to the crude storage tank. From storage it is fed to the heads column, where the low-boiling impurities (mostly dimethyl ether) are separated overhead (Stream 15) and sent either to another process or to a boiler as fuel. The bottoms from the heads column (Stream 16) go to the tails column, where purified methanol (Stream 17) is separated overhead and sent to the check tanks where it is held until checked for meeting specifications. High-boiling impurities (higher alcohols) are removed from the tails column as a sidestream (Stream 18) and sent to a boiler for use as fuel. The bottoms (Stream 19) from the tails column is the water separated from the crude methanol, and, since it contains only 100 to 300 ppm organics (mostly methanol), it is sent to a wastewater treatment system.[3–11]

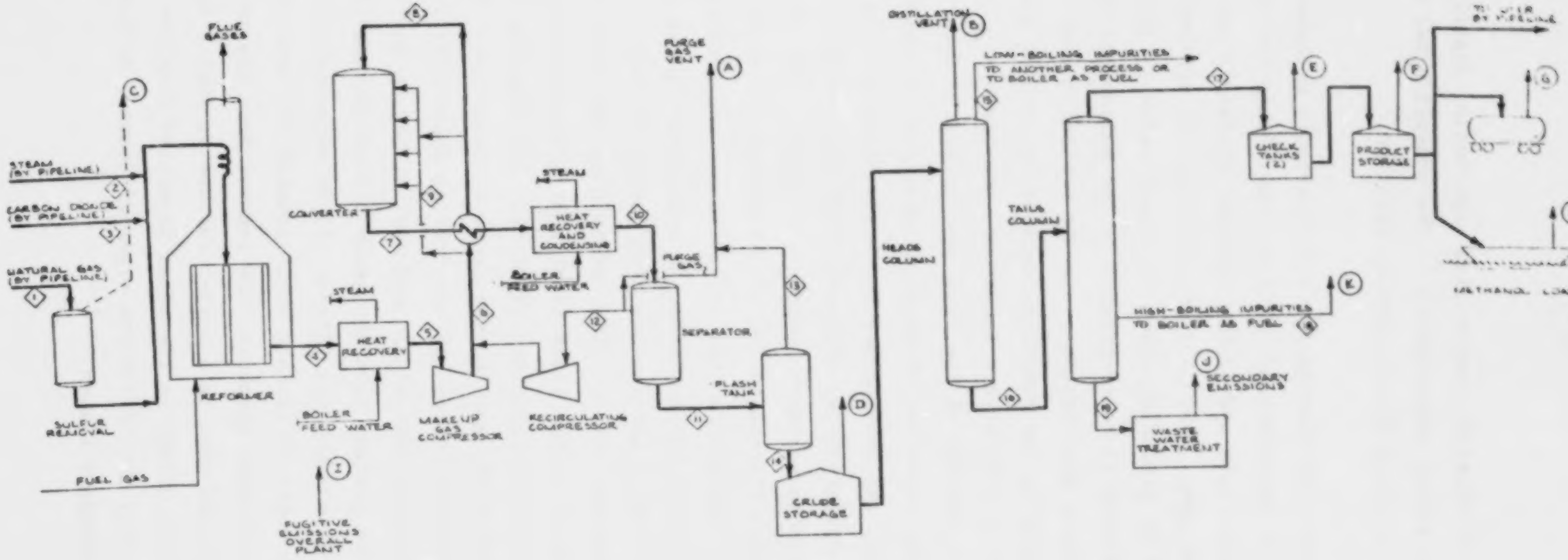

Fig. III-1. Flow Diagram for Uncontrolled Model Plant for Production of Methanol

The purge gas (Vent A) and the distillation section (Vent B) are sources of process emissions; in the sulfur removal section intermittent emissions can result from the regeneration of the activated carbon with steam (Vent C). The purge gas is usually burned, often in the reformer for its fuel value.[3–10]

Storage emission sources (Vents D through F) include crude storage, check tanks, and product storage. Handling emission sources (G and H) are the loading of methanol into railroad tank cars and into barges for shipment.

Fugitive emissions (I) occur when leaks develop in valves or in pump or compressor seals. When process pressures are higher than the cooling-water pressure, VOC can leak into the cooling water and escape as a fugitive emission from the cooling tower.

Secondary emissions can occur when wastewater containing VOC is sent to a wastewater treatment system or lagoon and the VOC are evaporated (J). Another source of secondary emissions is the combustion of liquid and gas waste streams in a boiler or process heater as fuel, where VOC are emitted with the flue gases (Vent K).[3–11]

C. PROCESS VARIATIONS[1,3–11]

In the model plant* carbon dioxide is added to provide the correct stoichiometric properties of carbon to hydrogen. One process variation involves the use of a larger purge gas flow to remove the excess hydrogen from the synthesis loop. Another process variation is the use of a shell and tube converter with boiling water in the shell to control the reaction temperature and produce steam. Other variations result from use of a different operating temperature of the converter and a different arrangement of the purification section. The high-pressure processes (28 to 45 MPa) were developed before the low-pressure processes were, and produce a crude methanol with more impurities. The high pressures are necessary to obtain commercially adequate reaction rates because the catalysts used are less active but more resistant to sulfur poisoning than those used in the low-pressure processes. The amount of water in the crude methanol is almost directly proportional to the amount of carbon dioxide converted to methanol. The number of distillation columns depends on the methanol specification that is to be met and can vary from one to three with several different arrangements and operating pressures.

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*See p I-2 for a discussion of model plants.

When partial oxidation of residual fuel oil is used to produce the synthesis gas, the pressure of the synthesis gas is high enough for a makeup gas compressor not to be required.

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IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. LOW-PRESSURE PROCESS

1. Model Plant*

The model plant for the low-pressure synthesis of methanol from natural gas (Fig. III-1) has a capacity of 450,000 Mg/yr, based on 8760 hr** of operation annually. The process and capacity are typical of those of recently built methanol plants and of one plant started up in 1980. Characteristics of the model plant important to air-dispersion modeling are shown in Table B-1 in Appendix B.

2. Sources and Emissions

Emissions sources and rates for the low-pressure process are summarized in Table IV-1. The process emissions estimated for the methanol model plant are based on information given in reports of visits to Borden,[1] Celanese,[2] and Monsanto[3] and in responses to EPA's requests for information from selected companies, together with data from a report published by Stanford Research Institute,[4] and on an understanding of the process chemistry and yields. The storage and handling emissions were calculated based on physical properties. The fugitive emissions are based on the petroleum refinery data referenced in Appendix C.

a. Purge Gas Vent——The purge gas vent (Vent A, Fig. III-1) is the largest process emission source. The vent gas contains the unreacted hydrogen, carbon monoxide, and carbon dioxide, the inert nitrogen and methane from the makeup synthesis gas, and small amounts of the uncondensed methanol and water vapor remaining after the crude methanol is condensed and separated. The composition of this stream depends on the makeup synthesis gas composition, the conversion catalyst, and the temperature and pressure in the converter. Flow and composition data on this stream were not available; the estimated composition of the vent gas from the model plant given in Table IV-2 is based on a material balance by Haddeland for a process employing carbon dioxide addition to the natural gas feed to the reformer. It was calculated by use of theoretical relationships for a methane conversion of about 90%, and does not represent the emissions from any specific plant or process. The estimate of the VOC emission rate given in Table IV-1 is based on the same data.[4]

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

b. Distillation Vent——The vent gases from the heads column (Vent B, Fig. III-1) are the noncondensables that are dissolved in the crude methanol fed to the column and the VOC that are not condensed, i.e., methanol, dimethyl ether, and methyl formate. The composition of the distillation vent gas from the model plant, shown in Table IV-3, is based on the reported composition from the distillation area vent of a methanol plant with a low-pressure synthesis process designed by ICI.[3] The estimate of the VOC emission rate given in Table IV-1 is based on the material balance by Haddeland,[4] the composition shown in Table IV-3, and on an estimate that 5% of the dimethyl ether is not condensed.

c. Sulfur Removal Vent——The natural gas feed to the model plant (Stream 1, Fig. III-1) normally contains no VOC and small amounts of sulfur compounds; as a result the intermittent emission (Vent C) during regeneration of the sulfur removal section contains no VOC, but only hydrogen sulfide, methane, and steam.[2,5] This vent can be a source of VOC emissions when the natural gas contains VOC that are adsorbed in the sulfur removal section and then desorbed during its steam regeneration.[6,7]

d. Storage and Handling Emissions——Emissions result from the storage of crude and purified methanol. Sources for the model plant are shown in Fig. III-1 (sources D through F). Storage tank parameters for the model plant are given in Table IV-4. The uncontrolled storage emissions in Table IV-1 were calculated and are based on fixed-roof tanks, half full, with an 11°C diurnal temperature variation.

Table IV-1. Total Uncontrolled VOC Emissions for Methanol Model Plant[a]

Source	Vent Designation (Fig.III-1)	Emissions Ratio (g/kg)[b]	Emissions Rate (kg/hr)
Purge gas vent	A	1.1	56.5
Distillation vent	B	0.4	20.5
Sulfur removal	C	c	c
Storage vents			
Crude methanol	D	0.0097	0.50
Check tanks[d]	E	0.080	4.1
Product	F	0.365	18.8
Handling			
Loading tank cars	G	0.0486	2.49
Loading barges	H	0.0971	4.99
Fugitive	I	0.578	29.7
Secondary			
Wastewater treatment	J	0.00044	0.023
Waste organic as fuel	K	0.000060	0.0031
Total		2.68	138

[a] Uncontrolled emissions are emissions from a process for which there are no control devices other than those necessary for economical operation.

[b] g of emissions per kg of methanol produced.

[c] Model-plant emissions during the sulfur removal unit regeneration contain no VOC.

[d] Tanks for holding product until it is checked.

Table IV-2. Estimated Composition of Purge Gas from Model Plant[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Methanol (VOC)	0.8	1.1
Methane	64.8	88.1
Hydrogen	15.1	20.6
Carbon monoxide	11.1	15.1
Nitrogen	4.9	6.7
Carbon dioxide	3.1	4.2
Water	0.2	0.2
Total	100	136

[a] See ref 4.

[b] g of emission per kg of methanol produced.

Table IV-3. Composition of Distillation Vent Gas from Model Plant*

Component	Composition (wt %)
Methanol	29.0
Dimethyl ether and methyl formate	12.1
Total VOC	41.1
Carbon dioxide	58.6
Water	0.3
Total	100

*See ref 3.

Table IV-4. Storage Tank Data for Methanol Model Plant

Parameter	Tank Crude	 Check[a]	 Product
Contents	Crude methanol	Methanol	Methanol
Number of tanks	1	2	2
Tank size (m^3)	1890	810	19,500
Turnovers per year	6[b]	350	15
Bulk temperature (°C)	27	27	27

[a] Tanks for holding product until it is checked.

[b] This tank operates at approximately constant level, and the number of turnovers indicated is an attempt to account for slight level variations.

Emission equations from AP-42 were used with one modification. The breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing-loss equation overpredicts emissions.[8,9]

Handling emissions result from the loading of methanol into railroad tank cars and into barges for shipment (sources G and H). These emissions are shown in Table IV-1 and were calculated with the equations from AP-42, based on submerged loading of methanol at 27°C and on one third of the production being shipped in tank cars and two thirds in barges.[10]

e. Fugitive Emissions——Process pumps, compressors, valves, and pressure-relief devices are potential sources of fugitive emissions (source I). The model plant is estimated to have 30 pumps, 1 compressor (with 2 seals), 1400 process valves, and 40 pressure relief devices handling VOC.[1--3] Half of the process valves and pressure-relief devices are in gas/vapor service. Pumps, compressors, valves, and pressure-relief valves not handling VOC (this includes the makeup gas compressor) are not included in these estimates. The fugitive emission factors from Appendix C were applied to these estimates, and the results are shown in Table IV-1 as fugitive emissions.

f. Secondary Emissions——Secondary VOC emissions can result from the handling and disposal of process waste streams. For the model plant two potential sources are indicated on the flow diagram (sources J and K, Fig. III-1).

The secondary emissions from wastewater treatment (source J) were estimated by procedures that are discussed in a separate EPA report on secondary emissions.[11] The wastewater composition and flow rate were estimated based on data received from methanol producers.[3,6] A Henry's-law constant was then calculated for the vapor-liquid system under consideration, and the emission rate was estimated by comparison with information given in existing literature.[11] This emission rate is shown in Table IV-1.

The boiler flue gas secondary VOC emissions, originating from waste organics used as fuel, were calculated with the emission factors from AP-42 for distillate oil combustion.[12] The basis for estimating the amount of high-boiling impurities and low-boiling impurities burned as fuel in a boiler for the model plant was a crude methanol composition from a low-pressure process given by Hiller and Marschner.[13] If the low-boiling impurities are sent to another process rather than burned as fuel as in the model plant, this estimated amount would be lower and therefore the calculated emissions would be lower. The secondary emissions from burning waste organics as fuel (Vent K, Table IV-1) were based on burning both low- and high-boiling impurities.

B. PROCESS VARIATIONS

It is reported that a high hydrogen—to—carbon monoxide ratio, which will result when natural gas is steam reformed without carbon dioxide addition, suppresses the undesirable side reactions but requires an increased purge gas flow to remove the excess hydrogen.[13,14] Data were not available on the effect, if any, that this has on the VOC emissions.

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7. W. P. Anderson, Tenneco Chemicals, letter dated May 10, 1978, to EPA with information on air emissions from the methanol plant at Pasadena, TX, in response to EPA request.

8. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-1—4.3-16 in Compilation of Air Pollutant Emission Factors, 3d ed., Part A, AP-42, EPA, Research Triangle Park, NC (April 1977).

9. E. C. Pulaski, TRW, Inc., letter dated May 30, 1979 to Richard Burr, EPA.

10. C. C. Masser, "Transportation and Marketing of Petroleum Liquids," op. cit., pp. 4.4-1—4.4-6.

11. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPQ/ESED report, Research Triangle Park, NC).

12. T. Lahre, "Fuel Oil Combustion," pp. 1.3-1—1.3-5 in Compilation of Air Pollutant Emission Factors, 3d ed., Part A, AP-42, EPA, Research Triangle Park, NC (April 1977).

13. H. Hiller and F. Marschner, "Lurgi Makes Low-Pressure Methanol," Hydrocarbon Processing **49**(9), 281—285 (1970).

14. D. D. Mehta and W. W. Pan, "Purify Methanol This Way," Hydrocarbon Processing **50**(2), 115—120 (1971).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. LOW-PRESSURE PROCESS

1. Purge Gas Vent

Although the stream from the purge-gas vent is the largest uncontrolled process emission source (Vent A, Fig. III-1) in the model plant, it is normally controlled by being burned as fuel gas or by being transferred to another process to utilize the methane, hydrogen, or carbon monoxide in it.[1—7] With the increasing cost of energy, this is done primarily for economic reasons. The control option selected for the purge gas in the model plant is the use of it as fuel gas in the reformer, which is economically justified by recovery of its value as fuel. The controlled VOC emissions in the reformer flue gas that originated in the purge gas (see Table V-1) were calculated by applying the emission factors from AP-42 for natural gas burned in an industrial process boiler,[8] and results in a VOC emission reduction of 98.2%.*

A flare is used by some plants to control the purge gas when for some reason it cannot be used as fuel.[3,6] The flare for a methanol plant would normally be designed for process emergency venting conditions. When the purge gas is burned in such a flare, the VOC destruction efficiency can be lower than 98%**.[9]

2. Distillation Vent

The control option selected for the model-plant distillation vent is the flare used to safely dispose of emergency releases in a methanol plant. A VOC reduction of 98%** was used to calculate the controlled emissions from the flare that originated in the distillation vent, based on the estimate that the vent gases from the distillation vent are greater than 10% of the maximum smokeless design flow for the flare.[9]

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*The destruction of the VOC entering the reformer is greater than 99.98%,[9] but after the VOC produced during combustion of the methane, hydrogen, etc. in the purge gas (which are not considered to be VOC) is taken into account, the net destruction efficiency is only 98.2%.

**Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies cited are for tentative comparison purposes.

Table V-1. VOC Controlled Emissions for Methanol Model Plant

Source	Vent Designation (Fig.III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Emissions Ratio (g/kg)[a]	VOC Emissions Rate (kg/hr)
Purge gas vent	A	Used as fuel	98.2	0.019	0.99
Distillation vent	B	Flare	98	0.008	0.41
Sulfur removal	C	None		b	b
Storage vents					
Crude methanol	D	Internal-floating-roof tanks	85	0.0014	0.074
Check tanks[c]	E	Internal-floating-roof tanks	85	0.012	0.62
Product	F	Internal-floating-roof tanks	85	0.055	2.8
Handling					
Loading tank cars	G	Aqueous scrubber	99	0.000486	0.0249
Loading barges	H	Aqueous scrubber	99	0.000971	0.0499
Fugitive	I	Detection and correction of major leaks	80	0.116	5.9
Secondary					
Wastewater treatment	J	None		0.00044	0.023
Waste organic as fuel	K	None		0.000060	0.0031
Total				0.213	10.9

[a] g of emission per kg of methanol produced.

[b] Model-plant emissions during the sulfur removal unit regeneration contain no VOC.

[c] Tanks for holding product until it is checked.

Another option used for control of the VOC in the distillation vent gases is to send them to the fuel gas system[3], either with or without a compressor, depending on the pressures involved. Usually this approach is justified by the economics of recovering the fuel value of the vent gases. The VOC reduction efficiency may be slightly better than that of a flare, but the difference in the controlled VOC emissions is minor.

3. Sulfur Removal Vent

No control option has been identified for this vent (Vent C) in the model plant because no VOC are emitted. Plants that do emit VOC during the regeneration of their sulfur removal system do not report any control devices, likely because the small amount of VOC and the sulfur compounds present make this a difficult control problem.[1,4,7]

4. Storage and Handling Emissions

The emissions from the model-plant storage tanks are controlled by use of internal-floating-roof tanks.* Options for control of storage and handling emissions are covered in another EPA report.[10]

The VOC emissions from loading tank cars and barges are controlled by aqueous scrubbers in the model plant. Aqueous scrubbers are used in similar applications to control emissions from methanol storage tanks, with the scrubber effluent sent to the crude methanol storage tank so that the methanol scrubbed from the vent gases is recovered.[2]

The controlled storage emissions given in Table V-1 were calculated on the assumption that a contact type of internal floating roof with secondary seals will reduce fixed-roof-tank emissions by 85%.[11,12] A VOC (methanol) removal efficiency of 99%, was used to calculate the controlled emissions from loading tank cars and barges for the model plant (see Table V-1). Calculation of removal efficiencies for once-through absorbers is discussed in Control Device Evaluation. Gas Absorption.[13]

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*Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

5. Fugitive Emissions

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry will be discussed in another EPA report.[14] Emissions from pumps and valves can be controlled by an appropriate inspection system and repair as needed. Controlled fugitive emissions calculated with the factors given in Appendix C are included in Table V-1; these factors are based on the assumption that major leaks are detected and corrected.

6. Secondary Emissions

a. Wastewater Treatment——Calculations based on estimated wastewater flow rates and compositions for the model plant indicate that the VOC emissions from the wastewater treatment (source J) are relatively small. No control system has been identified for the model plant. Control of secondary emissions are discussed in another EPA report.[15]

b. Waste Organic as Fuel——Estimates of the VOC emissions in the flue gases of the model plant reformer that originate in the waste organic streams used as fuel (source K) indicate they are very small. No control system has been identified for the model plant.

B. PROCESS VARIATIONS

The applicable controls for the high-pressure processes or for the processes where carbon dioxide is not added are the same as those for the low-pressure model plant.

C. REFERENCES*

1. R. L. Duggan, Air Products and Chemicals Inc., letter dated May 11, 1978, to EPA with information on air emissions from the methanol plant at Pensacola, FL, in response to EPA request.

2. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Borden, Geismar, LA, Mar. 3, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Celanese, Bishop, TX, Oct. 11, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. D. W. Smith, E. I. du Pont de Nemours and Company, letter dated May 25, 1978, to EPA with information on air emissions from the methanol plant at Beaumont, TX, in response to EPA request.

5. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Monsanto, Texas City, TX, Dec. 13, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

6. D. A. Copeland, Rohm and Haas Texas Incorporated, letter dated May 19, 1978, to EPA with information on air emissions from the methanol plant at Deer Park, TX, in response to EPA request.

7. W. P. Anderson, Tenneco Chemicals, letter dated May 10, 1978, to EPA with information on air emissions from the methanol plant at Pasadena, TX, in response to EPA request.

8. T. Lahre, "Natural Gas Combustion," pp. 1.41—1.4-3 in Compilation of Air Pollutant Emission Factors, 3d ed., Part A, AP-42, EPA, Research Triangle Park, NC (May 1974).

9. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

10. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC)

11. C. C. Masser, "Storage of Petroleum Liquids," Sect. 4.3 in Compilation of Air Pollutant Emission Factors, 3d ed., Part A, AP-42, EPA, Research Triangle Park, NC (April 1977).

12. W. T. Moody, TRW, Inc., letter dated Aug. 15, 1959, to D. A. Beck, EPA.

13. R. L. Standifer, IT Enviroscience, Inc., Control Device Evaluation. Gas Adsorption (October 1980) (EPA/ESED report, Research Triangle Park, NC).

14. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

15. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

1. Low Pressure Process

Table VI-1 shows the environmental impact of reducing the total VOC emissions by application of the described control systems (Sect. V) to the model plant described in Sects. III and IV. Use of these control devices or techniques results in the reduction of total VOC emissions by about 1100 Mg/yr for the model plant, and in the controlled emissions from the model plant being about 95 Mg/yr.

a. Purge Gas Vent——The use of purge gas as fuel reduces the model-plant VOC emissions by an estimated 486 Mg/yr and also reduces the natural gas needed as fuel, an increasingly important economic factor as the cost of natural gas increases. All domestic methanol producers normally use purge gas as fuel or as feed to another process (see Appendix D).

b. Distillation Vent——Sending the distillation vent gases to a flare reduces the model plant VOC emissions by 176 Mg/yr. A flare is needed to safely dispose of emergency releases from other parts of the methanol process.

c. Other Emissions (Storage, Handling, and Fugitive)——These sources are controlled in the model plant by internal-floating-roof storage tanks, aqueous scrubbers, and repair of leaking components for fugitive emissions. Application of these controls results in a VOC emission reduction of 448 Mg/yr for the model plant. Internal-floating-roof tanks for emission control neither consume energy nor have adverse environmental or energy impacts. The electrical energy and process water required for the aqueous scrubbers are negligible. The scrubbing water is returned to process for recovery of the methanol in it.

2. Process Variations

The environmental and energy inpacts of controlling the high-pressure processes and the processes where carbon dioxide is not added are similar to the impacts described for the low-pressure model plant.

Table VI-1. Environmental Impact of Controlled Methanol Model Plant

Emission Source	Vent Designation (Fig.III-1)	Control Device or Technique	VOC Emission Reduction (%)	VOC Emission Reduction (Mg/yr)
Purge gas vent	A	Used as fuel	98.2	486
Distillation vent	B	Flare	98	176
Sulfur removal	C	None		
Storage vents				
Crude methanol	D	Internal-floating-roof tanks	85	3.7
Check tanks*	E	Internal-floating-roof tanks	85	31
Product	F	Internal-floating-roof tanks	85	140
Handling				
Loading tank cars	G	Aqueous scrubber	99	22
Loading barges	H	Aqueous scrubber	99	43
Fugitive	I	Detection and repair of major leaks	80	208
Secondary				
Wastewater treatment	J	None		
Waste organic as fuel	K	None		
Total				1100

*Tanks for holding product until it is checked.

3. 1979 Industry Emissions

The total VOC emissions from the domestic methanol industry in 1979 are estimated to be 3000 Mg, and includes the estimated emissions from the process, fugitive, secondary, and storage and handling sources (see Appendix D).

B. CONTROL COST IMPACT

1. Process Vents

Use of the purge gas as fuel or as feed to another process is necessary if the plant is to be competitive economically; so there is no cost impact to providing this control. A flare is necessary in a methanol plant for safe disposal of emergency releases of flammable gases, and the cost impact of connecting the distillation vent to it or to an equivalent control is negligible when a new plant is being designed. The cost of retrofitting these controls to an existing plant may be appreciably greater than their cost for a new installation if there is some distance between the source and the existing control. No control has been identified for the sulfur removal vent.

2. Storage and Handling Sources

The control system for storage sources is the use of internal-floating-roof tanks. Aqueous scrubbers are used to control the model-plant methanol handling emissions from loading tank cars and barges. Another EPA report covers storage and handling emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[1]

3. Fugitive Sources

EPA fugitive emissions and their applicable controls are discussed in a separate EPA report.[2]

4. Secondary Sources

No control system has been identified for controlling the secondary emissions from wastewater treatment or from burning the waste organic streams as fuel. Another EPA report covers secondary emissions and their applicable controls.[3]

C. REFERENCES*

1. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

2. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

3. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Methanol is produced from synthesis gas, a mixture of hydrogen and carbon oxides, usually obtained by steam reforming of natural gas. The domestic production capacity of methanol for 1980 was estimated to be 4,310,000 Mg. Formaldehyde production consumes about 40% of the methanol produced. The estimated methanol consumption annual growth rate is 7%. When current new constructon and expansions are completed, capacity will be sufficient to satisfy domestic requirements beyond 1983.[1]

Emission sources and uncontrolled and controlled emission rates for the methanol model plant are given in Table VII-1. The major uncontrolled emission source is the purge gas vent; normally the purge gas is used as fuel or as feed to another process for economic reasons, therefore actual controlled emissions from the source are small. The emissions from the distillation vent can be flared in the plant flare system designed for safe disposal of emergency releases of flammable gases. VOC emissions from the sulfur removal system vent during regeneration are minor or nonexistent, depending on the amount of VOC in the natural gas used as feed.

The model-plant methanol storage emissions are controlled by internal-floating-roof tanks, and the emissions from loading tank cars and barges by aqueous scrubbers. Potential secondary emissions are minor. The total methanol industry VOC emissions are estimated at 3000 Mg in 1979, with most of the uncontrolled VOC emissions coming from fugitive, storage, and handling emissions.

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[1] A. D. Abshire, et al., "Methanol," pp. 674.5021A—I and 674.5022A—674.5026A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1980).

Table VII-1 Emission Summary for Methanol Model Plant
(450,000 Mg/yr)

Emission	Vent Designation (Fig.III-1)	VOC Emission Rate (kg/hr) Uncontrolled	VOC Emission Rate (kg/hr) Controlled
Purge gas vent	A	56.5	0.99
Distillation vent	B	20.5	0.41
Sulfur removal	C	a	a
Storage vents			
Crude methanol	D	0.50	0.074
Check tanks[b]	E	4.1	0.62
Product	F	18.8	2.8
Handling			
Loading tank cars	G	2.49	0.0249
Loading barges	H	4.99	0.0499
Fugitive	I	29.7	5.9
Secondary			
Wastewater treatment	J	0.023	0.023
Waste organics as fuel	K	0.0031	0.0031
Total		138	10.9

[a] Model-plant emissions during the sulfur removal unit regeneration contain no VOC.

[b] Tanks for holding product until it is checked.

APPENDIX A

Table A-1. Physical Properties of Methanol*

Synonyms	Methyl alcohol, carbinol, methyl hydroxide
Molecular formula	CH_4O
Molecular weight	32.04
Physical state	Liquid
Vapor pressure	127.9 mm Hg at 25°C
Vapor specific gravity	1.11
Boiling point	64.8°C at 760 mm Hg
Melting point	-93.9°C
Density	0.7913 g/ml at 20°C/4°C
Water solubility	Soluble

*From: J. Dorigan _et al._, "Methyl Alcohol," p. AIII-154 in _Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N)_, Rev. 1, Appendix III, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properies of Dimethyl Ether*

Synonyms	Methyl ether, methyl oxide, methoxymethane
Molecular formula	C_2H_6O
Molecular weight	46.07
Physical state	Gas
Vapor pressure	4551.3 mm Hg at 25°C
Vapor specific gravity	1.59
Boiling point	-23.7°C at 760 mm Hg
Melting point	-138.5°C
Density	0.661 g/ml
Water solubility	74,000 mg/liter of H_2O

*From: J. Dorigan et al., "Dimethyl Ether," p AII-144 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals D—E), Rev 1, Appendix II MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-3. Physical Properties of Methyl Formate*

Synonyms	Methyl ester of formic acid, methyl methanoate
Molecular formula	$C_2H_4O_2$
Molecular weight	60.05
Physical state	Liquid
Vapor pressure	602.5 mm Hg at 25°C
Vapor specific gravity	2.07
Boiling point	32.0°C at 760 mm Hg
Melting point	-99°C
Density	0.975 g/ml at 20°C/4°C
Water solubility	Soluble

*From: J. Dorigan _et_ _al_., "Methyl Formate," p AIII-194 in _Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F—N)_, Rev 1, Appendix III, MTR-7248, MITRE Corp., McLean, VA (September 1976).

APPENDIX B

Table B-1. Air-Dispersion Parameters for Model Plant with a Capacity of 450,000 Mg/yr

Source	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled Emissions			
Purge gas vent	15.7	20	0.6	320	6.3	22
Distillation vent	5.7	20	0.1	320	0.0092	1.2
Storage vents						
Crude methanol	0.14	12.2	14	300		
Check tanks (2)	0.57 (each)	9.8	10.3	300		
Product (2)	2.6 (each)	14.6	41.2	300		
Handling						
Loading tank cars	0.69	4	0.5	300		
Loading barges	1.4	2	0.5	300		
Fugitive[a]	8.2					
Secondary						
Wastewater treatment	0.0063	1	30	300		
Waste organic as fuel	0.00086	30	16	450	90	4.5
			Controlled Emissions			
Purge gas vent[b]	0.28					
Flare (distillation vent)	0.11	60	0.5	1250		
Storage						
Crude methanol	0.021	12.2	14	300		
Check tanks (2)	0.086 (each)	9.8	10.3	300		
Product (2)	0.39 (each)	14.6	41.2	300		
Aqueous scrubber (loading emissions)	0.021	5	0.3	300	0.063	0.9
Fugitive[a]	1.64					

[a] Fugitive emissions are distributed over an area of 150 m X 400 m.

[b] Vent used as fuel gas.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

EXISTING PLANT CONSIDERATIONS

A. 1979 INDUSTRY EMISSIONS

The total VOC emissions from the domestic methanol industry in 1979 are estimated to be 3000 Mg, and includes the estimated emissions from the process, fugitive, secondary, and storage and handling sources. This estimate is based on an estimated 1979 level of production of 3,400,000 Mg, calculated by applying the estimated future 7% growth per year (see Sect. II) to the reported production for 1977[1] and from the emission ratios from Tables IV-1 and V-1, together with an estimate of the percentage of production associated with controlled and with uncontrolled emissions in each category. These estimates are based on engineering judgement, on data from individual methanol producers,[1—7] on state and local emission control agencies, and on the open literature. The following individual estimated projections were made:

Source	1979 VOC Emissions (Mg/yr)
Process	250
Storage and handling	1700
Fugitive	1200
Secondary	2
Total (rounded)	3000

The sources of the largest amounts of VOC emissions are storage and handling and fugitive emissions. Since the retrofit of controls to these sources, that is, internal-floating-roof tanks, vent scrubbers, or refrigerated vent condensers for tanks and inspection of equipment for fugitive emissions, is often cost effective, many producers are working to do so. Refrigerated vent condensers are reportedly more economical to retrofit to existing tanks and only slightly less efficient than internal floating roofs or scrubbers.[8—9]

Data comparing the uncontrolled VOC emissions from a Rohm and Haas methanol plant using a high-pressure process with those estimated for the model plant low-pressure plant were included in the draft version of this report but have been removed because this plant no longer exists.[10]

B. EXISTING PLANT CHARACTERIZATION

Table D-1 lists emission control devices reported in use by industry. To gather information for the preparation of this report three site visits were made to producers of methanol. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, Research Triangle Park, NC.[2,3,5] Other sources of information in this appendix are letters in response to requests by EPA for information on emissions from methanol plants.[1,4,6,7]

1. Air Products, Pensacola, FL[1]

The following data on process emissions were supplied:

a. Distillation Condenser Vent——This is a vent of noncondensibles form the vent condenser on the methanol distillation column. Most of this stream is recovered and sent to the boilers. Excess gas that cannot be handled by the vent compressor is vented to the atmosphere.

Flow	0.86 acfm	
Temperature	90°F	
Methanol emissions	1.2 lb/hr	4.81 tons/yr

b. Synthesis Vent—This vent is used infrequently and emits methanol synthesis gas just upstream of the converter loop. It is used only during startups and shutdowns.

Flow	248 acfm	
Temperature	80°F	
Emissions		
H_2	58.4 lb/hr	234 tons/yr
CO	68.5 lb/hr	275 tons/yr
CH_4	41.5 lb/yr	166 tons/yr

c. Organic Sulfur Removal Unit Regeneration Vent (Intermittent)——This vent is used intermittently end the vent gases are comprised of steam and traces of sulfur. High-pressure steam is used to regenerate the catalyst beds in organic sulfur removal twice per week.

Table D-1. Emission Control Devices or Techniques Currently Used by Some Methanol Producers

Source	Control Devices or Techniques Used						
	By Air Products[a]	By Borden[b]	By Celanese[c]	By Du Pont[d]	By Monsanto[e]	By Rohm & Haas[f]	By Tenneco[g]
Purge gas vent	Transferred to another process; flash gas scrubbed and sent to boiler	Transferred to another process or to reformer fuel gas	To fuel gas with flare alternate	To fuel gas most of the time	To fuel gas or to reformer	To fuel gas with flare alternate	To fuel gas
Distillation vent	Compressed and sent to boiler; excess vented to atmosphere	Transferred to another process; pure column vented to atmosphere	To fuel gas	Compressed and sent to fuel gas[h]	Flare	Flare	Compressed and sent to fuel gas
Storage vents							
Crude methanol	None	Aqueous scrubber	Floating roof	Compressed by ejectors to fuel gas; motive gas is purge gas	None	Flare	Not reported
Product	None	Aqueous scrubber	Floating roof or to flare	None	Internal floating roof[h]	Internal floating roof	None
Handling	Not reported	None	To another process	None	None	Not applicable (used on site)	Not reported

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[a] See ref 1.

[b] See ref 2.

[c] See ref 3.

[d] See ref 4.

[e] See ref 5; this plant is no longer in existance (ref 10).

[f] See ref 6.

[g] See ref 7.

[h] Some vents go directly to the atmosphere. Monsanto reports that they are on a program to install internal floating roofs and to reduce storage vent emissions to the atmosphere (see ref

Flow	823 acfm	
Temperature	450°F	
H_2S emissions	1.47 lb/hr	0.18 tons/yr

2. Borden, Geismar, LA[2,11]
The methanol "B" plant uses Chemico high-pressure technology and was started up in 1967. Since the site visit, Borden has been replacing this process with ICI low-pressure technology and is expecting to start up the revamped and expanded plant by the end of 1980.

3. Celanese, Bishop, TX[3]
The methanol synthesis uses Lurgi low-pressure technology and was started up in 1976.

4. Du Pont, Beaumont, TX[4]
The following data on process emissions were supplied:

a. Natural Gas Desulfurizer Regeneration Vent——This vent removes sulfur compounds from activated carbon catalyst during regeneration of catalyst with steam (340 hr/yr).

Flow	825 lb/hr
Composition, wt%	
H_2S	0.1
CH_4	10.9
C_2H_6, C_3H_8, C_4H_{10}	0.4
H_2O	88.6
Temperature, °C	100

b. Reactor Vent——This vent removes inert gases from the reactor system during periods when there is no CO_2 in the feed (approximately 35 days per year).

Flow	15,000 lb/hr
Composition, wt %	
H_2	36.0
CO	35.0
CO_2	15.0
CH_4	10.5
N_2	3.0
CH_3OH, H_2O and dimethyl ether	0.5
Temperature, °C	40 to 50

The above data were determined from composition analysis of purge stream and estimated flow to the atmosphere. During periods when CO_2 is being fed to the reformer, this stream is burned as fuel in the reformer without being vented to the atmosphere.

c. Reformer Process Vents (2)——These vents discharge process gas from the reformer during startup and shutdown operations. There is no discharge during normal operation.

Flow	128,600 lb/hr
Composition, wt %	
H_2	16.3
CH_4	2.3
CO_2	39.6
CO	41.8
Temperature, °C	120

The above data were determined by gas analysis.

d. Dehydrator Column Vent——This vent emits noncondensable gases from the condenser.

Flow	4 lb/hr
Composition, wt %	
CH_3OH	85
N_2	15
Temperature, °C	66

The above data were determined by calculations based on operating conditions.

e. Splitter Column Vent——This vent emits low-boiling organics during plant startup, shutdown, or process upsets.

Flow	5850 lb/hr
Composition, wt %	
Dimethyl ether	62
Ch_3OH	37
Methyl formate, methylal, acetone	1
Temperature, °C	55

The above data were determined by calculation based on operating conditions and flow measurements. Emissions are normally compressed and burned in the reformer. Only during startup, shutdown, or compressor shutdown are there any emissions to atmosphere.

5. Tenneco, Pasadena, TX

The following data on process emissions were supplied:

a. Compressor Interstage Knockout Vent——This vent provides liquid-vapor separation during compression of synthesis gas.

Flow	202 scfm
Composition, %	
H_2O	83
CO	17
MeOH	0.001
Temperature, °F	87

b. Desulfurizer Carbon-Bed Vent (Regeneration)——Activated carbon adsorbes sulfur compounds from natural gas prior to reforming. Carbon must be regenerated with steam periodically to restore activity.

Flow	Intermittent (during regeneration only)
Total emissions, tons/yr	
H_2O	580
CH_4	130
Ethane	16
Propane	24
i-Butane	16
n-butane	21
Temperature, °F	420 max.

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11. A. D. Abshire *et al*., "Methanol," pp 674.5021A—674.5021I and 674.5022A--674.5026A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1980).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 3

ETHYLENE

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Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

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This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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CONTENTS OF REPORT 3

		Page
I.	ABBREVIATIONS AND CONVERSION FACTORS	I-1
II.	INDUSTRY DESCRIPTION	II-1
	A. Ethylene (Olefins)	II-1
	B. Ethylene Usage and Growth	II-1
	C. Domestic Producers	II-4
	D. References	II-8
III.	PROCESS DESCRIPTION	III-1
	A. Introduction	III-1
	B. Naphtha/Gas-Oil Process	III-3
	C. Process Variations	III-11
	D. New Processes	III-19
	E. Foreign Processes	III-20
	F. References	III-21
IV.	EMISSIONS	IV-1
	A. Current Pyrolysis Processes	IV-1
	B. Other Processes	IV-23
	C. References	IV-24
V.	APPLICABLE CONTROL SYSTEMS	V-1
	A. Current Pyrolysis Processes	V-1
	B. Other Processes	V-17
	C. References	V-18
VI.	IMPACT ANALYSIS	VI-1
	A. Control Cost Impact	VI-1
	B. Environmental and Energy Impacts	VI-12
	C. Reference	VI-17
VII.	SUMMARY	VII-1

APPENDICES OF REPORT 3

		Page
A.	PHYSICAL PROPERTIES OF FEEDSTOCKS AND PRODUCTS	A-1
B.	AIR-DISPERSION PARAMETERS (MODELS III AND VII)	B-1
C.	FUGITIVE-EMISSION FACTORS	C-1
D.	COST ESTIMATE DETAILS	D-1
E.	INTERMITTENT-EMISSION SAMPLE CALCULATIONS	E-1
F.	SALT-DOME STORAGE-EMISSION SAMPLE CALCULATIONS	F-1
G.	LIST OF EPA INFORMATION SOURCES	G-1
H.	EXISTING PLANT CONSIDERATIONS	H-1

TABLES OF REPORT 3

Table No.		Page
II-1	Feed Requirements and Co-Product Yields from Various Feedstocks	II-2
II-2	Ethylene Usage and Growth Rate	II-3
II-3	Producers and Plant Locations	II-5
II-4	New Plants--Locations, Feedstocks, Capacities	II-7
III-1	Estimated Material Losses Due to Compressor Outages	III-18
IV-1	Capacity Data for Plants Using Various Feedstocks	IV-2
IV-2	Production from Various Feedstock Combinations	IV-3
IV-3	Benzene and VOC Uncontrolled Emissions for Model-Plants I-II	IV-5
IV-4	Benzene and VOC Uncontrolled Emissions for Model-Plants III-IV	IV-6
IV-5	Benzene and VOC Uncontrolled Emissions for Model-Plants V-VI	IV-7
IV-6	Benzene and VOC Uncontrolled Emissions for Model-Plants VII-VIII	IV-8
IV-7	Benzene and VOC Uncontrolled Emissions for Model-Plants IX-X	IV-9
IV-8	Assumed Charge Gas Composition from Model Plants	IV-16
IV-9	Atmospheric Storage Tank Conditions	IV-20
IV-10	Wastewater Parameters	IV-22
V-1	Benzene and VOC Controlled Emissions for Model-Plant I	V-2
V-2	Benzene and VOC Controlled Emissions for Model-Plant II	V-3
V-3	Benzene and VOC Controlled Emissions for Model-Plant III	V-4
V-4	Benzene and VOC Controlled Emissions for Model-Plant IV	V-5
V-5	Benzene and VOC Controlled Emissions for Model-Plant V	V-6
V-6	Benzene and VOC Controlled Emissions for Model-Plant VI	V-7

Tables (continued)

Table No.		Page
V-7	Benzene and VOC Controlled Emissions for Model-Plant VII	V-8
V-8	Benzene and VOC Controlled Emissions for Model-Plant VIII	V-9
V-9	Benzene and VOC Controlled Emissions for Model-Plant IX	V-10
V-10	Benzene and VOC Controlled Emissions for Model-Plant X	V-11
VI-1	Cost Factors Used in Computing Annual Costs	VI-2
VI-2	Cost and Cost Effectiveness for Model-Plant Flares	VI-3
VI-3	Environmental Impact of Controlled Model-Plant III	VI-13
VI-4	Environmental Impact of Controlled Model-Plant VIII	VI-14
VII-1	Emission Summary for Model-Plant III	VII-2
VII-2	Emission Summary for Model-Plant VIII	VII-2
VII-3	Composite Model-Plant Emissions Summary	VII-3
VII-4	Estimated Emissions for the Industry	VII-5
VII-5	Cost Effectiveness Ratios for Model-Plants III & VIII	VII-5

FIGURES OF REPORT 3

Figure No. Page

II-1 Locations of Plants Manufacturing Ethylene II-6

III-1 Process Flow Diagram for Plant with Naphtha/Gas-Oil Feed III-4

III-2 Process Flow Diagram for Process with Ethane/Propane Feed III-12

IV-1 Total Uncontrolled VOC Emissions vs Plant Capacity IV-10

IV-2 Uncontrolled Benzene Emissions vs Plant Capacity IV-12

V-1 Total Controlled VOC Emissions vs Plant Capacity V-12

V-2 Total Controlled Benzene Emissions vs Plant Capacity V-14

VI-1 Capital Cost of Flare Options vs Plant Capacity for Intermittent Emission Control Model-Plants I-X VI-5

VI-2 Cost Effectiveness of Flare Options vs Plant Capacity for Control of Intermittent VOC Emissions VI-6

VI-3 Cost Effectiveness of Flare Options vs Plant Capacity for Control of Intermittent Benzene Emissions VI-8

VI-4 Capital Cost of Flares vs Plant Capacity for Model-Plants III Through V (50:50 E/P) VI-10

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. ETHYLENE (OLEFINS)

The production of ethylene, a basic building block for a large segment of the organic chemical industry, was selected for study because (1) it is produced in greater quantity than any other organic chemical,[1] (2) the total estimated emissions of VOC are relatively high, (3) significant expansion in ethylene production capacity is expected,[1--3] and (4) some processes emit significant quantities of benzene,[4] which was listed as a hazardous pollutant by EPA in the Federal Register on June 8, 1977.

Most ethylene is produced by the pyrolysis or thermal cracking of natural-gas concentrates (primarily ethane and propane) or the heavier petroleum liquids (primarily naphthas and atmospheric gas oils).

Propylene and 1,3-butadiene, formed with ethylene during pyrolysis, are generally recovered as co-products. Therefore, the processes producing ethylene are also termed "olefins" processes. Pyrolysis gasoline, another significant co-product, is a complex mixture of the C_5 and heavier compounds formed during pyrolysis, with benzene as a major component. When liquid petroleum feedstocks, such as naphthas and gas oils, are cracked, significant quantities of pyrolysis fuel oil are also produced.[2,5]

Emissions include all components present in the cracked gas (see Appendix A for pertinent physical properties of feedstocks and primary products). The cracked-gas composition and product yield structure are strongly dependent on the feedstocks used and on the thermal cracking conditions. Table II-1[1] shows typical feed requirements and co-product yields for plants annually producing 454 Gg (1 billion lb) of ethylene from several of the more common feedstocks.

B. ETHYLENE USAGE AND GROWTH

Table II-2 shows the major ethylene uses and expected growth rate. The predominant uses are for the manufacture of polyethylene, styrene, ethylene oxide, and vinyl chloride.[1]

Table II-1. Typical Feed Requirements and Co-Products Produced for Plants Producing 453.5 Gg/yr (1 Billion lb/yr) of Ethylene from Various Feedstocks[a]

		Co-Product Yields (Gg/yr) for 453.5-Gg/yr Ethylene Plants						
Feedstock	Feed Requirements (Gg/yr)	Hydrogen and Methane	Propylene	Total C_4 Mixture	Butadiene in C_4 Mixture	Pyrolysis Gasoline	Benzene in Pyrolysis Gasoline	Fuel Oil
Ethane (E)	551.7	66.1	11.2	13.2	9.2	7.3	3.4	0.4
Propane (P)	1030.6	295.2	165.1	45.5	30.4	61.8	26.8	9.4
50:50 E/P	791.1	180.7	88.1	29.4	19.8	34.5	15.1	4.9
Naphthas (N)	1439.2	225.8	205.5	137.6	66.8	307.7	83.4	109.0
Atmosphere, gas oils (G)	1774.3	211.7	269.2	169.8	82.8	324.0	96.8	346.1
50:50 N/G	1606.8	218.8	237.3	153.7	74.8	315.9	90.1	227.6

[a] Based on averages of ranges given in ref 1.

Table II-2. Ethylene Usage and Growth Rate[a]

End Use	Percent of Production (1979)	Projected Average Annual Percent Growth (1979—1984)
Low-density polyethylene	27.2	4.0—4.5
High-density polyethylene	17.5	6.0—6.5
Ethylene oxide	17.8	2.0—3.0
Vinyl chloride	11.9	6.0—7.0
Ethylbenzene, styrene	8.0	2.5—3.5
Ethyl alcohol	2.7	1.5—2.5
Aliphatic alochols	2.4	5.0—6.0
Acetaldehyde	2.3	(-5.0)—(-6.0)
Vinyl acetate	2.2	2.5—3.5
Ethyl chloride	1.0	(-7.0)—(-8.0)
Alpha olefins	2.1	6.5—7.5
Other	4.9	
	100.0	Avg. 4.0—4.5

[a] See ref 1.

Domestic ethylene production in 1979 was 13,200 Gg. The estimated production capacity at year's end was 16,500 Gg. Four new units and major expansions planned for 1980 and 1981 will increase the capacity to 18,600 Gg by the end of 1981. With a predicted annual growth rate of 4 to 4.5% the industry is expected to be operating at about 75% of capacity by the end of 1981.[1,6]

C. DOMESTIC PRODUCERS

As of 1979 twenty-five manufacturers were producing ethylene in the U.S. and Puerto Rico, at 36 locations. Table II-3 lists the producers and the feedstocks used and Fig. II-1 shows the plant locations.

The bulk of the increase in capacity is taking place on the Texas side of the Gulf Coast. Table II-4 lists the producers, plant locations, and expected feedstocks for the new plants or significant expansions expected to be completed in 1980 and 1981.

With the increasing scarcity and higher cost of natural-gas liquids, almost all new capacity planned after 1978 will use heavy-liquid feedstocks, primarily naphthas and atmospheric gas oils.[1,2,6] By 1981, 42 to 47% of U.S. ethylene production is expected to be from heavy-liquid feeds, in contrast to 1969, when 90% was from natural-gas concentrates and refinery off-gases.[1] The shift to heavy- liquid feedstocks will result in the oil companies providing most of the expansion in ethylene capacity because petroleum refineries are generally the sources of these feedstocks, and large quantities of petroleum type of co-products, especially gasoline and fuel oil, are produced (see Table II-1 for comparative yield structures).[5]

Although very little expansion in ethylene capacity based on natural-gas concentrates is expected and even though a few of the older and less fuel-efficient plants may close between 1979 and 1981, the production of ethylene from natural-gas liquids is not expected to decrease appreciably during this period.[1]

Table II-3. Ethylene Producers as of 1979 and Their Plant Locations, Feedstocks, and Capacities[a]

Producing Company	Plant Location	Feedstock	Ethylene Production Capacity (Gg/yr)
Allied Chemical/BASF Wyandotte/Borg-Warner	Geismar, LA	Ethane, propane	336
Atlantic Richfield (Arco)	Channelview, TX	Naphtha, gas oil	1,179
Atlantic Richfield (Arco)	Wilmington, CA	Refinery off-gas, ethane, propane	45
Chemplex	Clinton, IO	Ethane, propane	238
Cities Service	Lake Charles, LA	Ethane, propane, butane	385
Continental Oil	Lake Charles, LA	Ethane	295
Dow Chemical	Freeport, TX	Ethane, propane	1,020
Dow Chemical	Plaquemine, LA	Ethane, propane	544
E. I. du Pont de Nemours	Orange, TX	Ethane, propane	374
Eastman Kodak	Longview, TX	Ethane, propane	576
El Paso Products/Rexene Polyolefins	Odessa, TX	Ethane, propane, butane	236
Exxon	Baton Rouge, LA	Ethane, propane, naphtha, gas oil	816
Exxon	Baytown, TX	Gas oil, naphtha	590
B.F. Goodrich	Calvert City, KY	Propane	159
Gulf Oil	Cedar Bayou, TX	Ethane, propane, naphtha, gas oil	730
Gulf Oil	Port Arthur, TX	Refinery off-gas	567
Mobil	Beaumont, TX	Naphtha, gas liquids, refinery off-gas	408
Monsanto	Alvin, TX	Field condensate naphtha, gas oil	295
Monsanto	Texas City, TX	Field condensate	45
National Distillers and Chemical	Tuscola, IL	Ethane	181
Internorth, Inc.	East Morris, IL	Ethane, propane, butane	408
Olin Corp.	Brandenburg, KY	Ethane	45
Phillips Petroleum	Sweeny, TX	Ethane, propane, butane	971
Shell Oil	Deer Park, TX	Ethane, propane, gas oil	1,270
Shell Oil	Norco, LA	Ethane, propane, heavy liquids	635
Standard Oil (Indiana)	Alvin, TX	Naphtha, gas liquids	907
Sun Company	Corpus Christi, TX	Refinery gas	9
Sunolin Chemical	Claymont, DL	Refinery gas, ethane, propane	102
Texaco	Port Arthur, TX	Naphtha, propane, butane	454
Texaco (Jefferson Chemical)	Port Neches, TX	Ethane, propane, refinery gas	238
Union Carbide	Seadrift, TX	Ethane, propane, crude oil	544
Union Carbide	Taft, LA	Naphtha, ethane, propane	526
Union Carbide	Texas City, TX	Ethane, propane	590
Union Carbide	Torrance, CA	Ethane, propane	75
Union Carbide	Penuelas, PR	Naphtha	454
U.S. Steel Corp.	Houston, TX	Refinery gas, ethane, propane	227
Total			16,474

[a] See ref 1.

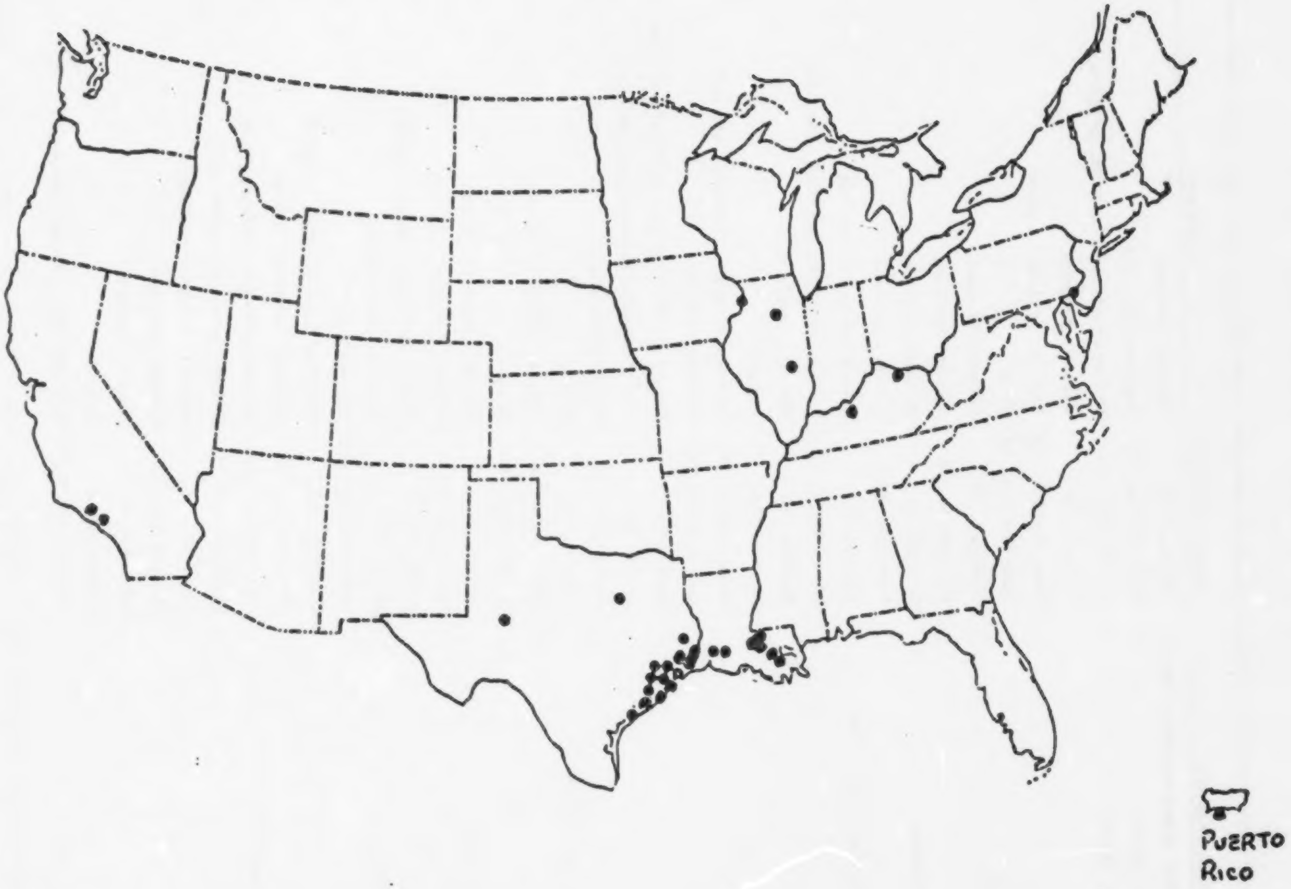

Fig. II-1. Locations of Plants Manufacturing Ethylene (ref 1.
(See Table II-3 for specific plant and location designations.)

Table II-4. New Ethylene Plants (Expected to Be Completed Between 1980-1981), Their Locations, Feedstocks, and Capacities[a]

Producing Company	Plant Location	Feedstock	Ethylene Production Capacity (Gg/yr)
Dow	Plaquemine, LA	Naphtha	454
Corpus Christi Petrochemicals	Corpus Christi, TX	Naphtha	544
Conoco/Monsanto	Chocolate Bayou, TX	Naphtha	680[b]
Shell	Norco, LA	Gas oil	680

[a] See ref 1.

[b] Includes capacity of Monsanto's existing plant, which will be integrated into new plant.

D. REFERENCES*

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6. "U.S. Ethylene Capacity: Too Much of a Good Thing?" Chemical Engineering 85(7), 80, 81 (1978).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Almost all commercial ethylene is produced by pyrolysis of natural-gas concentrates and petroleum fractions. Although significant amounts of ethylene were once extracted from by-product petroleum refinery streams (40% of the U.S. production in 1956), only about 2% of the current ethylene production is derived from this source. Most of the plants that are extracting ethylene from refinery streams also produce ethylene by pyrolysis.[1,2]

Several alternative pyrolysis processes, primarily utilizing feedstocks not currently in common use, are either being commercially attempted on a limited scale or are in the development stage with expectations of limited commercial application between 1980 and 1985. Although these processes are all expected to be commercially proven within 5 years, wide application will depend on demonstrated favorable process economics. No significant impact on total olefins production is anticipated from these developmental processes for at least 10 years.[2]

The primary difference between the domestic and foreign olefins industries has been in the feedstocks used for pyrolysis. In Japan and Europe natural-gas liquids have historically been scarce and naphtha has been the predominant feedstock.[2]

The pyrolysis reaction mechanisms by which ethylene and co-products are formed are very complex, particularly for the heavier feedstocks. The simplest example of ethylene formation is the following free-radical sequence for ethane:[2]

Initiation	$C_2H_6 \rightarrow (CH_3)^* + (CH_3)^*$
Propagation	$(CH_3)^* + C_2H_6 \rightarrow CH_4 + (C_2H_5)^*$
Propagation	$(C_2H_5)^* \rightarrow C_2H_4 + (H)^*$
Propagation	$(H)^* + C_2H_6 \rightarrow H_2 + (C_2H_5)^*$

(Note: The asterisk denotes a free radical.)

The reactions are highly endothermic. Favorable conditions include a high temperature, a low pressure, and the presence of steam. In most current commercial processes, pyrolysis is accomplished noncatalytically, inside radiantly heated tubes. Optimum ethylene yields require a short residence time at pyrolytic temperatures, followed by rapid quenching. Additional process operations are required for removing water and undesirable impurities and for separating the product fractions.[2,3]

Although all pyrolysis processes are alike in these basic requirements, there are many specific process variations. The 35 domestic plant locations have at least 60 separate process units, which have been built over a time span of 40 years.[1,2] Generally each unit was custom-designed to satisfy specific requirements and was based on the prevailing technology, economic conditions, and regulatory requirements.

The most notable variations in relatively recent pyrolysis processes stem from variations in feed composition. Since product yield structure and process requirements depend strongly on feed composition, pyrolysis processes are designed for specific feedstocks or combinations and generally cannot be operated efficiently if there is much deviation from the design feed ranges.[2,4] Although a variety of specific feedstocks and combinations are used, the most prevalent pyrolysis processes can be classified as those using natural-gas concentrates and refinery off-gases, composed primarily of ethane, propane, and butane (E/P processes); and those using heavy petroleum-based liquids, primarily naphthas and atmospheric gas oils (N/G processes).[2,3]

Among the newer commercial processes, variations are much less significant. Most new processes (1978 and later) have the following common characteristics:

1. Heavy-liquid feedstocks (primarily naphthas and atmospheric gas oils) -- As is shown in Table II-4, all significant new capacity projected for 1980 or later will use naphthas and gas oils.

2. High capacity -- Most new units will produce from 450 to 680 Gg of ethylene per year. Most smaller capacity increases will involve the expansion of existing facilities (see Table II-4).

3. Separation of product fractions by low-temperature distillation -- Although low-temperature distillation has been the most common separation method for many years, several older processes use selective absorption or adsorption.[3]

4. Large-equipment and single-train operation -- Most newer olefins processes are composed of a single process train and minimize the use of multiple, parallel, major items of equipment. This trend has been most notable with the increased use of large centrifugal compressors and larger fractionation towers.[5]

B. NAPHTHA/GAS-OIL PROCESS

The process flow diagram shown in Fig. III-1 represents a recent process for naphtha and/or atmospheric gas-oil feedstocks,[3,6,7] the projected feedstocks for almost all new ethylene capacity. Processes using natural-gas liquids (E/P processes) are generally similar but less complex, with fewer and much smaller quantities of co-products obtained (see Sect. III.C).

Naphtha and/or gas oil (Stream 1), diluted with steam, is fed in parallel to a number of gas- or oil-fired tubular pyrolysis furnaces. The fuel gas and oil (Stream 2) for these furnaces are supplied from gas and oil fractions removed from the cracked gas in subsequent separation steps. In cracking naphtha and/or gas oil, the ratio of steam to feed must be high for optimum yields and minimal formation of coke in the reactor tubes. Ethane and propane, which are present in the cracked gas and are separated in subsequent distillation steps (Streams 35 and 38), are combined and recycled (Stream 3) through a separate cracking furnace. The resulting cracked gas is combined with the cracked gas from the naphtha/gas-oil furnaces (Stream 5). The flue gas from the pyrolysis furnaces is vented (Vent A). During operation, coke accumulates on the inside walls of the reactor coils, and each furnace must be periodically taken out of service for removal of the accumulated coke. Normally one furnace is out of service for decoking at all times. Decoking is accomplished by passing steam and air through the coil while the furnace is maintained at an elevated temperature, effectively burning the carbon out of the coil. While a furnace is being decoked, the exhaust is diverted (Stream 7) to an emission control device (Vent B) whose primary function is to reduce particulate emissions. The collected particles are removed as a slurry

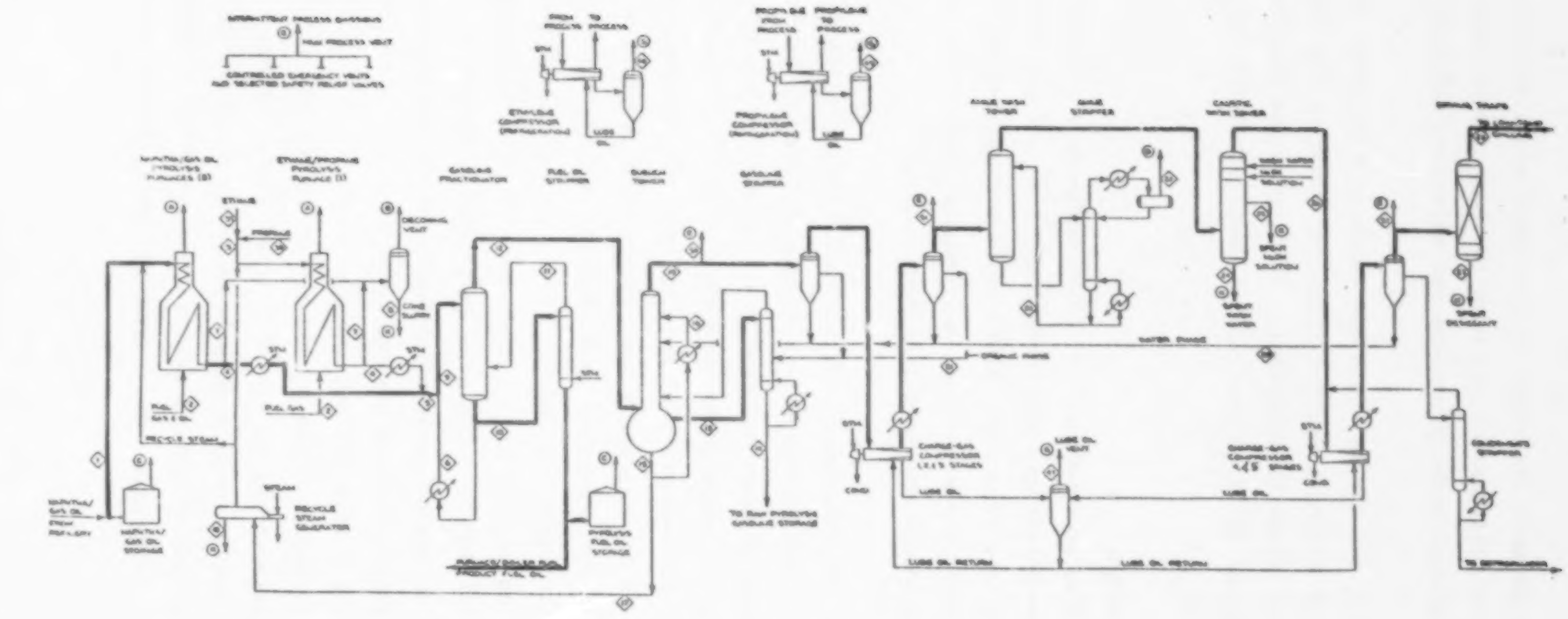


Fig. III-1. Process Flow Diagram for Naphtha and/or Gas-Oil Feeds

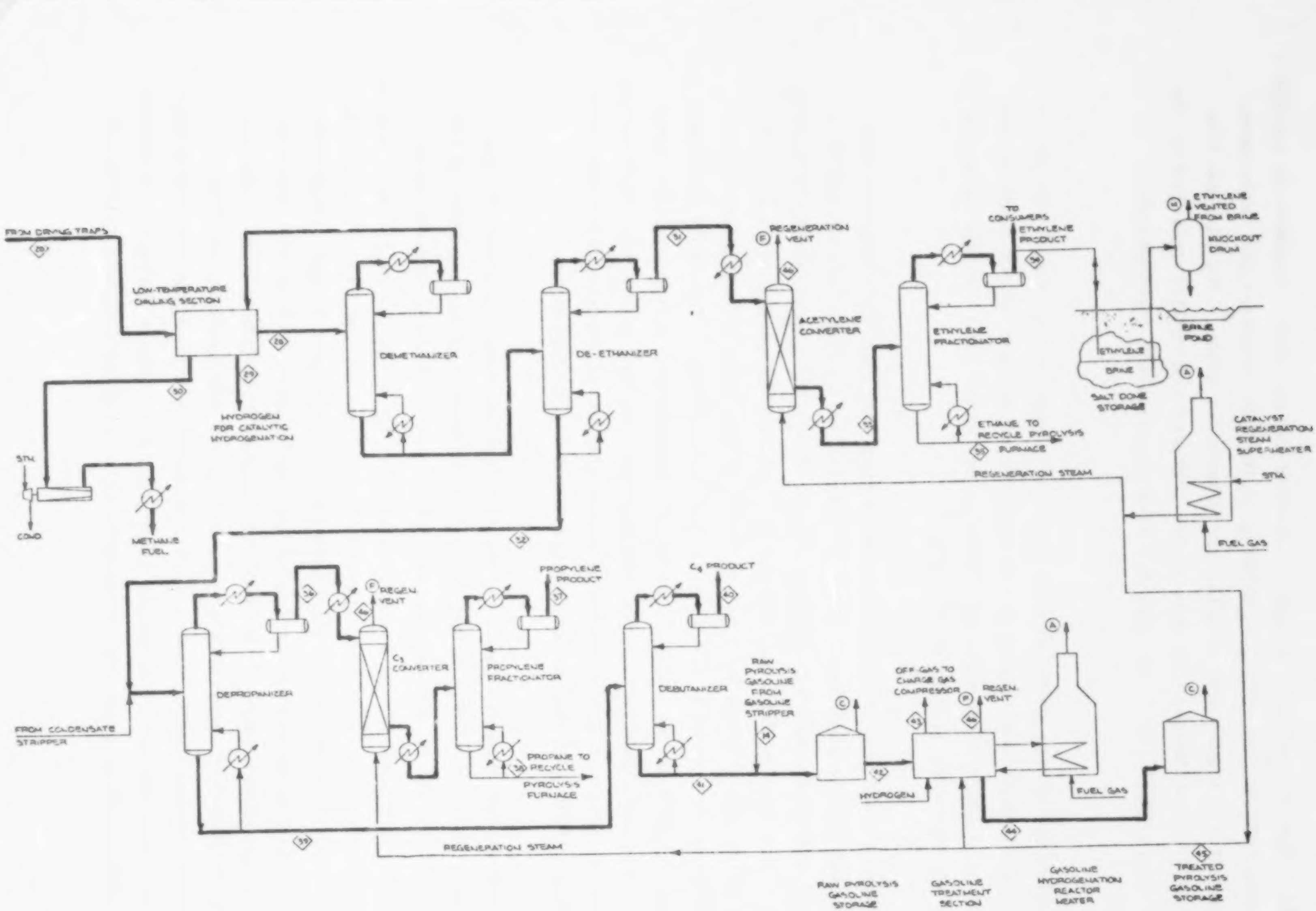


Fig. III-1. (Continued)

(Stream 8). The cracked gas (Stream 4) leaving the pyrolysis furnaces is rapidly cooled (quenched) to 250--300°C by passing it through transfer-line exchangers,[7] which terminate pyrolysis and simultaneously generate steam. The streams from the transfer-line exchangers (Stream 5) are combined and further quenched by the injection of recycled pyrolysis fuel oil from the gasoline fractionator (Stream 6).

The remaining operations shown on Fig. III-1 are required for separation of the various product fractions formed in the cracking of gas oil and/or naphtha, for removal of acid gases (primarily H_2S and CO_2) and water, and for hydrogenation of acetylene compounds to olefins or paraffins.

The quenched cracked gas (Stream 9) passes to the gasoline fractionator, where pyrolysis fuel oil is separated. Most of the fuel oil passes through water-cooled heat exchangers and is recycled (Stream 6) to the preceding oil-quenching operation. The surplus fuel oil (Stream 10), equivalent to the quantity initially present in the cracked gas, passes first to the fuel oil stripper, where light fractions are removed, and then to fuel oil storage. The light fractions (Stream 11) removed in the fuel oil stripper are recycled to the gasoline fractionator. The gasoline fractionator temperatures are well above the vaporization temperature of water, and the contained water remains as superheated steam, with the overhead stream containing the lighter cracked-gas components.

The overhead stream from the gasoline fractionator (Stream 12) passes to the quench tower, where the temperature is further reduced, condensing most of the water and part of the C_5 and heavier compounds. The condensed organic phase (Stream 13) is stripped of the lighter components in the gasoline stripper and is passed to raw pyrolysis gasoline intermediate storage (Stream 14). Most of the water phase, which is saturated with organics, is separated in the quench tower (Stream 15), passed through water-cooled heat exchangers (Stream 16), and then recycled to the quench tower to provide the necessary quench cooling. The surplus water (Stream 17), approximately equivalent to the quantity of steam injected with the pyrolysis furnace feed, passes to the dilution steam generator,[7] where it is vaporized and recycled as steam to the pyrolysis furnaces. Blowdown from the recycle steam generator is removed as a wastewater stream (Stream 18).

The overhead stream from the quench tower (Stream 19) passes to a centrifugal charge-gas compressor (first three stages), where it is compressed to approximately 1.5 MPa. Water (Stream 20) and organic fractions (Stream 21) condensed during compression and cooling are recycled to the quench tower and gasoline stripper.

Lubricating oil (seal oil) discharged from the charge-gas compressor is stripped of volatile organics in a separator pot before the oil is recirculated. The organic vapor is vented to atmosphere (Vent G). Similar separator pots separate volatile organics from lubricating oil from ethylene and propylene refrigeration compressors (Streams 48 and 49).

Following compression, acid gas (H_2S, CO_2) is removed by absorption in diethanolamine (DEA) or other similar solvents in the amine wash tower followed by a caustic wash step. The amine stripper strips the acid gas (Stream 22) from the saturated DEA and the DEA (Stream 23) is recycled to the amine wash tower. Very little blowdown from the DEA cycle is required.

The waste caustic solution, blowdown from the DEA cycle, and wastewater from the caustic wash tower are neutralized, stripped of acid gas, and removed as liquid-waste streams (Streams 24 and 25). The acid gas stripped from the DEA and caustic waste (Stream 22) passes to an emission control device (Vent D), primarily to control H_2S emissions.

Following acid gas removal, the remaining process gas stream (Stream 26) is further compressed to approximately 3.5--4 MPa (Stages 4 and 5) and is then passed through drying traps that contain a desiccant, where the water content is reduced to the low level necessary to prevent ice or hydrate formation in the low-temperature distillation operations. The drying traps are operated on a cyclic basis, with periodic regeneration necessary to remove accumulated water from the desiccant. The desiccant is regenerated with heated fuel gas (not shown), and the effluent gas is routed to the fuel system. Fouling of the desiccant by polymer formation necessitates periodic replacement, which results in the generation of a solid waste (Stream 27); however, with normal desiccant service life (possibly several years) this waste source is relatively minor.

With the exception of three catalytic hydrogenation operations, the remaining process steps involve a series of fractionations in which the various product fractions are successively separated.

The demethanizer separates a mixture of hydrogen and methane from the C_2 and heavier components of the process gas (Stream 28). The demethanizer overhead stream (hydrogen and methane) is further separated into hydrogen-rich and methane-rich streams (Streams 29 and 30) in the low-temperature chilling section. The methane-rich stream is used primarily for furnace fuel. Hydrogen is required in the catalytic hydrogenation operations.

The de-ethanizer separated the C_2 components (ethylene, ethane, and acetylene) (Stream 31) from the C_3 and heavier components (Stream 32). Following catalytic hydrogenation of acetylene to ethylene by the acetylene converter (Stream 33), the ethylene-ethane split is made by the ethylene fractionator. The overhead from the ethylene fractionator (Stream 34) is removed as the purified ethylene product, and the ethane fraction (Stream 35) is recycled to the ethane/propane cracking furnace.

The de-ethanizer bottoms (C_3 and heavier compounds) (Stream 32) pass to the depropanizer, where a C_3-C_4 split is made. The depropanizer overhead stream (primarily propylene and propane) (Stream 36) passes to a catalytic hydrogenation reactor (C_3 converter), where traces of propadiene and methyl acetylene are hydrogenated. Following hydrogenation, the C_3 fraction passes to the propylene fractionator, where propylene is removed overhead as a purified product (Stream 37). The propane (Stream 38) is recycled to the ethane/propane pyrolysis furnace.

The C_4 and heavier components (Stream 39) from the depropanizer pass to the debutanizer, where a C_4-C_5 split is made. The overhead C_4 stream (Stream 40) is removed as feed to a separate butadiene process.

The stream containing C_5 and heavier compounds from the debutanizer (Stream 41) is combined with the bottoms fraction from the gasoline stripper (Stream 14) as raw pyrolysis gasoline. The combined stream (Stream 42) is hydrogenated in the gasoline treatment section. Following the stripping of lights (Stream 43), which are recycled to the cracked-gas compressor, the C_5 and heavier compounds (Stream 44) are transferred to storage as treated pyrolysis gasoline. This stream contains benzene and other aromatics formed by pyrolysis.

To meet the low-temperature requirements of most of the fractionation columns, liquid ethylene and propylene are used as refrigerants. A significant part of the process equipment is included in the refrigeration cycles. These cycles consist of centrifugal propylene and ethylene compressors, a complex of flash tanks, condensers, and heat exchangers, all of which are necessary to attain the required low temperatures and to efficiently utilize the refrigeration. As the only normal process emissions from the refrigeration cycles are from the ethylene and propylene compressor lubricating oil vents (Streams 48 and 49), the refrigeration cycles are not included in the flowsheet.

The three catalytic hydrogenation reactors for acetylene, C_3 compounds, and pyrolysis gasoline all require periodic regeneration of the catalyst to remove contaminants. The catalyst is generally regenerated every four to six months. At the start of regeneration, as superheated steam (Stream 45) is passed through a reactor, a mixture of steam and hydrocarbons leaving the reactor (Stream 46) is passed to the quench tower (arrow not shown). After sufficient time has elapsed for stripping of malodorous organics (approximately 48 hr), the exhaust is directed to an atmospheric vent (Vent F) and a steam-air mixture is passed through the catalyst to remove residual carbon. This operation continues for an additional 24 to 48 hr. The presence of air during this phase of the regeneration prevents the vented vapor from being returned to the process.

Emissions from the gasoline hydrogenation reactor heater (Vent A) and the catalyst regeneration steam superheater (Vent A) are composed of flue gas formed from the combustion of gaseous fuel.

The process described in this section is characterized by very low VOC emissions from process vents during normal operation, with only one minor benzene emission source (charge-gas compressor lubricating oil vent, Stream 47, Vent G).

Most process emissons of VOC occur during abnormal conditions, such as scheduled startups and shutdowns, process upsets, and emergency situations. Emissions result from the activation of pressure-relief devices, the intentional venting of off-specification materials, and the depressurization and purging of equipment in preparation for maintenance. The greatest quantity of intermittent emissions results from outages of the refrigeration and charge-gas compressors. Although compressor outages are relatively infrequent and of short-term duration, the resultant high rates cause significant quantities of VOC emissions, including benzene. With the exception of the demethanizer relief valves, which may vent directly to the atmosphere (not shown), all pressure-relief devices and controlled emergency vents are routed through the main process vent (Vent E) to an emission-control device. Emissions resulting from activation of demethanizer relief valves are infrequent and are composed primarily of hydrogen and methane.

Fugitive emissions can contain all components present in the cracked gas, including benzene. The extreme variation in composition throughout the process produces widely varying compositions of fugitive emissions. As with most organic chemical processes, leaks into cooling water can occur, allowing volatile organic compounds (VOC) to escape.

Storage-tank emission sources (labeled C on Fig. III-1) include naphtha, gas oil, pyrolysis fuel oil, and pyrolysis gasoline. Primary storage of ethylene is in pressurized underground salt domes. Emissions that occur when dissolved VOC is stripped from salt brine displaced from the storage domes are vented (Vent H). Since feedstock and products are transferred by pipeline, handling emissions are not significant.

The five potential sources of secondary emissions (labeled K on Fig. III-1) are (1) blowdown from the dilution steam generator, (2) spent caustic, (3) wash water from the caustic wash tower, (4) coke generated from pyrolysis furnace and transfer line exchanger decoking, and (5) spent desiccant from the process gas dryers. The coke is composed of uncombined carbon containing organics with very high molecular weights, and secondary emissions are very low. Secondary emissions from spent desiccant are insignificant since the organics remaining after steam purging of the traps have high molecular weights and desiccant replacement is infrequent (approximately every 4 or 5 years).

C. PROCESS VARIATIONS

With more than 60 domestic process units, constructed over a time span of approximately 40 years[1,2] and frequently designed to satisfy individual requirements, variations in commercial ethylene processes are numerous. The most significant variations and their effects on VOC emissions are summarized below:

1. Feedstock Composition

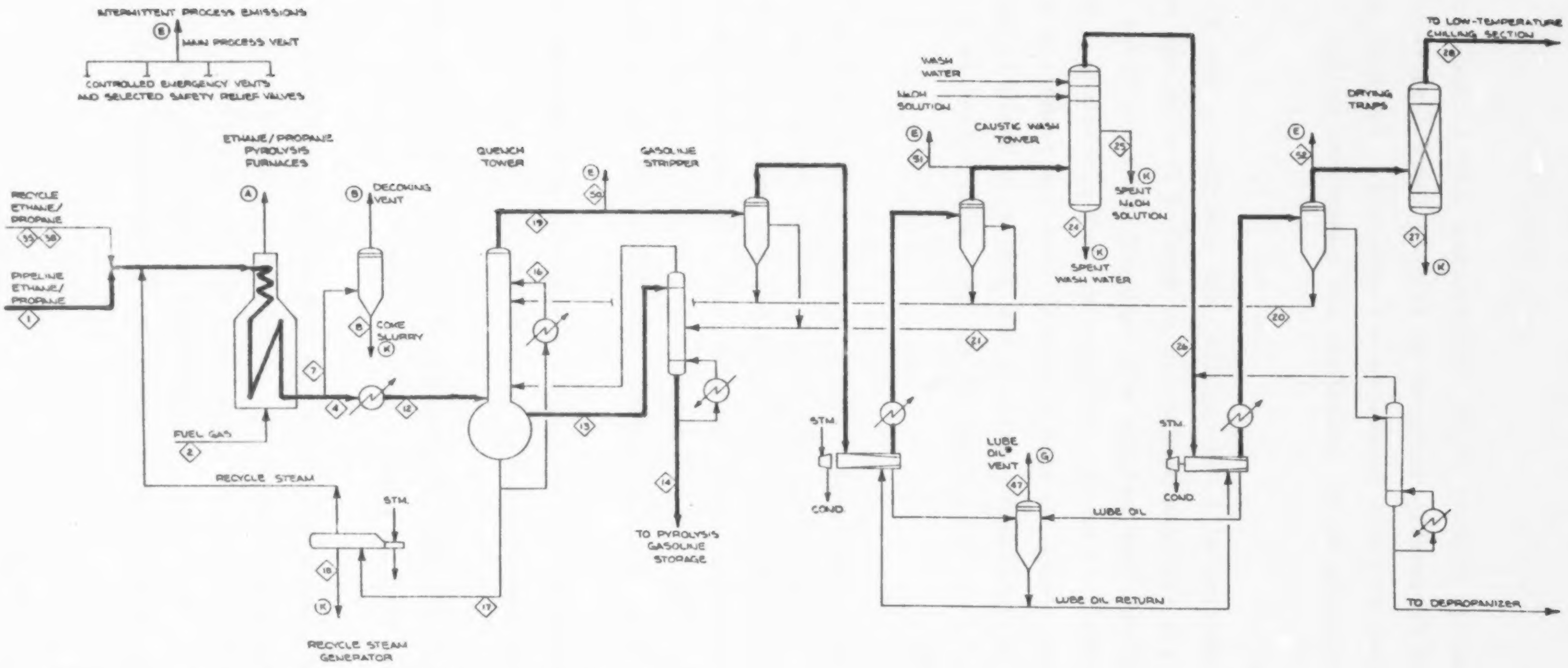
Most new ethylene production will use naphthas and atmospheric gas oils as feedstocks, but most current ethylene production is derived from ethane and propane. Although various feedstock combinations are employed, most processes use either heavy liquids (N/G processes) or gas concentrates (E/P processes). Butane and naphtha are supplemental feeds in some processes that use primarily ethane and propane feedstocks. Heavy-liquid processes are generally designed for either naphtha or gas oil or for a combination of the two, with butane as a relatively minor supplemental feed.

a. Ethane-Propane Feed (E/P Processes) -- The E/P process shown in Fig. III-2[2,3,8] is similar to the N/G process (Fig. III-1) but is less complex. All process steps and stream designations shown on Fig. III-2 are included in Fig. III-1 with identical stream and emission source designations. Stream and emission sources designated in Fig. III-1 for the N/G process that do not occur in the E/P process (Fig. III-2) are omitted. The E/P process simplifications are as follows:

1. A gasoline fractionator and fuel oil stripper are not included because essentially no pyrolysis fuel oil is produced (see Table II-1).

2. The cracked gas is not partially quenched by oil. It is entirely quenched in transfer line exchangers and a quench tower.

3. Since the sulfur content of ethane and propane obtained from natural-gas concentrates generally is very low, an MEA tower may not be included. The smaller quantities of acid gas (H_2S, CO_2) may be removed by caustic scrubbing alone. H_2S or SO_2 emissions, a significant problem with heavier feedstocks (particularly gas oils), are not generally a significant problem with E/P processes.



* - IDENTICAL LUBE OIL VENT SYSTEMS FOR ETHYLENE, PROPYLENE, AND METHANE COMPRESSORS NOT SHOWN

Fig. III-2. Flow Diagram for Ethane-Propane Feed Process

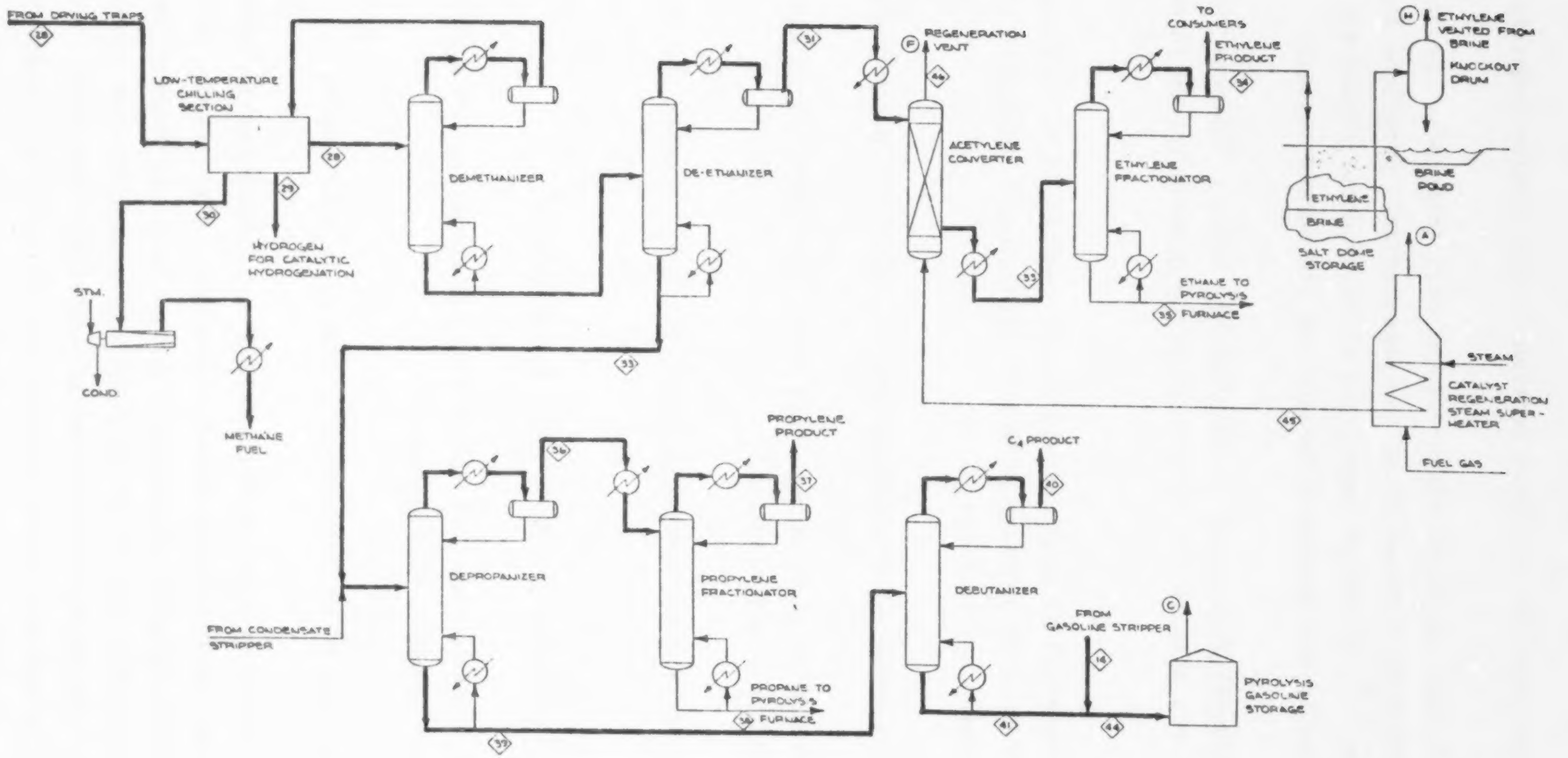


Fig. III-2. (Continued)

4. A pyrolysis gasoline treatment section is not usually required.[3,8]

In the simplest case, in which ethane is the sole feedstock, the process may be further simplified by elimination of the depropanizer, propylene fractionator, and debutanizer.[2,8] The small quantities of co-products formed are not separated but are recycled to the pyrolysis furnaces or are burned as fuel.

b. Effects of Feedstock Variations -- Increasingly heavy feedstocks (progressing from ethane to gas oil) result in the following general trends in process characteristics:

1. More raw material is required and larger quantities of co-products are formed per unit of ethylene produced, resulting in increased process capacity requirements (see Table II-1).
2. The process becomes increasingly complex, with more process steps required.[8]
3. Shorter residence time, higher heat flux, and higher steam dilution ratios during pyrolysis are required.[2]
4. The quantity of coke formed during pyrolysis is greater and decoking is more frequent.[2]
5. The quantity of process wastewater is increased.[2]
6. Operating problems caused by heavy-residue formation are more severe, resulting in more frequent maintenance.[2]
7. The sulfur content of feedstocks is generally much higher.[2]

Although the process variations described do not significantly affect direct process emissions of VOC during normal operation, intermittent, fugitive, and secondary VOC emissions are potentially greater with the heavier feedstocks because of the greater quantities of materials processed, the increased process complexity, and the greater quantities of wastewater generated. With higher concentrations of benzene in the cracked gas, intermittent, fugitive and secondary emissions of benzene are significantly greater with the heavier feedstocks.

Storage tank emissions are generally less from E/P processes.[2] Atmospheric tanks, used for naphtha, gas oil, and pyrolysis fuel oil storage when heavy-liquid feeds are used, are not used and pyrolysis gasoline storage requirements are less. Ethane and propane are generally received by pipeline and are either fed directly to the pyrolysis furnaces or stored in pressure vessels. Vapor vented from pressurized storage vessels is also introduced as pyrolysis furnace feed.

2. Cracked-Gas Quenching and Quench-Water Treatment

Variations in the methods of quenching the cracked gas and in the cooling, handling, and disposal of effluent water from quenching operations result in significant variations in VOC emissions. The most significant variations, prevalent primarily in older processes, can result in relatively large quantities of VOC and benzene emissions. Effluent quench water is potentially a significant VOC and benzene emission source. The water is saturated with the organic compounds present in the cracked gas at the quench-tower operating pressure (approximately 200 kPa), and will release organic vapor if the pressure is reduced as it is discharged. Because benzene is a relatively high-boiling cracked-gas component, the proportion of benzene in the organics emitted from quench water is significantly higher than the benzene concentration in the cracked gas.

Very significant VOC emissions from quench water have been reported[9] for older processes in which (1) the hot quench water was discharged directly to vented, atmospheric, settling basins, where organic residues were separated; and (2) the effluent water from the settling basins was then passed through cooling towers before being recycled to the quench tower, effectively stripping and venting most of the remaining organics. In one case combined VOC emissions of more than 400 kg/hr from both sources were initially reported. The reported emissions in this case were subsequently reduced by approximately 90% with the installation of a vacuum stripping tower. In the revised process the quench-tower effluent water passes through the stripping tower before it is discharged to the settling basins, and the stripped vapor is recycled to the quench tower or is incinerated.

There are no significant emissions from recycled quench water in the process shown in Fig. III-1 because (1) phase separation is attained in the quench tower base, thereby eliminating venting of the contained vapor, and (2) the process water is cooled in water-cooled heat exchangers. When heat exchangers are used, the cooling water that subsequently passes through cooling towers does not contact process organics.

In most older processes the excess quench water effluent, which results from the addition of dilution steam in the pyrolysis furnaces, is not recycled as dilution steam but is removed as a wastewater stream. The quantity of wastewater resulting from steam dilution is potentially greater when heavy-liquid feedstocks are used because higher ratios of steam to feed are necessary.

Some older processes do not utilize transfer line exchangers for primary quenching.[3,9] The primary purpose of transfer line exchangers is to improve process thermal efficiency. Emissions are only indirectly affected. When transfer line exchangers are not used, two variations are: a two-stage quench system composed of a primary oil-quench, followed by a water-quench step; or quenching solely with water. With a total water quench the greater amounts of water used may result in increased emissions from the discharged quench water.

3. Compressors

In contrast to recent processes that primarily utilize high-capacity, single-train, centrifugal compressors[10] (typically equipped with high-efficiency, oil-purged mechanical seals),[11] many older processes use larger numbers of lower capacity compressors operated in parallel. As a result of the larger number of compressors and the use of either reciprocating compressors or older centrifugal compressors with less efficient seals, compressor fugitive emissions are typically greater than those from the more recent processes.

Intermittent process emissions caused by compressor outages are typically much greater with single compressor trains than with parallel dual or multiple trains.[10] A compressor shutdown will result in the venting of process material, generally to a flare.

The quantity of material vented depends on the venting rate and the time required to re-establish stable operation. When a compressor outage occurs, the venting rate is much less with dual compressor trains and the return to stable operation is much more rapid. The emergency shutdown of one of two parallel compressors does not interrupt the other machine, and product purity at a production rate of 50% of capacity can be maintained.

The specific compressor that trips (e.g., charge gas, propylene, ethylene) affects the quantity of material vented. Generally charge-gas compressor outages are much more frequent than refrigeration compressor outages.

The estimated material losses caused by compressor outages for single- and dual-train plants experienced by one producer are shown in Table III-1.[10] Losses were estimated for the first 5 years of operation, from plants producing 450-Gg/yr ethylene from naphtha/gas-oil feeds. Losses resulting from compressor outages tended to decrease during the first 5 years of operation, because operating problems were eliminated and compressor reliability improved, becoming relatively constant after the fifth year. Atmospheric emissions resulting from these losses depend on the efficiency of the emission-control devices.

4. Raw Material and Product Transfer

Although pipeline transfer of all raw materials and products is widely used, shipment of heavier products (i.e., propylene, crude butadiene, pyrolysis fuel oil, pyrolysis gasoline) by tank car, tank truck, and barge is also common. When methods other than pipeline transfer are used, potential emissions are significantly greater. Other methods for transferring ethylene are relatively rare and are generally used only for relatively small quantities of ethylene.[1]

5. Integration of Related Processes

The ethylene (olefins) process shown in Fig. III-1 does not include the separation of 1,3-butadiene from the C_4 fraction nor the separation of C_5 compounds, benzene, toluene, and xylene contained in pyrolysis gasoline. Although generally performed in separate process units, in some cases these operations are included as integral operations within the olefins units.[3]

6. Separation of Other Product Fractions

Acetylene may be removed as a separate product by an absorption-stripping operation instead of eliminating it by catalytic hydrogenation. Other variations include separating pyrolysis fuel oil into two or more fractions, separating the C_5 fraction from pyrolysis gasoline, and removing propane as a product instead of recycling to pyrolysis.

Table III-1. Estimated Material Losses Due to Compressor Outages[a]
(453.5 Gg/yr Ethylene, N/G Feed)

Outages and Material Losses	Year of Operation 1	2	3	4	5
			Single Compressor Trains		
Annual trips and checks	10	7	6	5	4
Material lost per trip, Mg	816	816	816	816	816
Annual compressor maintenance	3	2	1	1	1
Material lost per occurrence, Mg	571	571	571	571	571
Total material lost, Mg	9878	6857	5469	4653	3837
Cost at raw-material value ($1000)	1180	820	650	560	460
			Dual Compressor Trains		
Annual trips and checks	20	14	12	10	8
Material lost per trip, Mg	61	61	61	61	61
Annual compressor maintenance	6	4	2	2	2
Material lost per occurrence, Mg	0	0	0	0	0
Total material lost, Mg	1224	857	735	612	490
Cost at raw-material value ($1000)	150	100	90	70	60

[a] See ref 10.

7. Refrigerants and Refrigeration Cycles

The type of refrigerants used varies, as do the number of levels of refrigeration and the refrigeration cycle equipment configurations. Alternative refrigerants include propane, methane, and ethane. The refrigerants are almost invariably pyrolysis gas components.

8. Miscellaneous Process Variations

Other process variations that have relatively minor effects on emissions are

1. separation of products by selective absorption or adsorption instead of low-temperature fractionation,
2. variation in the order of some process steps, including charge-gas compression, acid-gas removal, water removal, acetylene hydrogenation, and product fraction separations,
3. variations in fractionation tower conditions (i.e., pressure, temperature, reflux ratios),
4. use of other processes or solvents for the removal of acid gases.

D. NEW PROCESSES

Pyrolysis processes primarily using feedstocks not currently in common use for the production of olefins are being commercially attempted on a limited scale or are in the development stage, with expectations of limited commercial application between 1980 and 1985.[2] Wider application will depend on demonstrated favorable process economics, and no significant impact on total olefins production is anticipated for at least 10 years. Such processes are conventional pyrolysis of vacuum gas oil (Exxon), autothermic pyrolysis of crude oil (Union Carbide/Kureha), fluid-bed pyrolysis of petroleum residues (AIST), and fluid-bed pyrolysis of coal (Garret Corp.).

The preliminary nature of these processes makes specific emission data unavailable. Variations from current processes are primarily in the pyrolysis steps, with generally similar separation and purification steps. Following the general trends of heavier feedstocks, VOC emissions are probably slightly higher than from current atmospheric gas-oil processes.[2]

E. FOREIGN PROCESSES

In most foreign commercial ethylene processes, liquid petroleum feedstocks are used primarily. Processes are generally similar to domestic naphtha/gas-oil processes.[2] The alternative processes discussed in the preceding section include both domestic and foreign developments.

F. REFERENCES*

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11. W. E. Nelson, "Compressor Seal Fundamentals," *Hydrocarbon Processing* **56**(12), 91--95 (1977).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

A. CURRENT PYROLYSIS PROCESSES

1. Model Plants

Current operating ethylene plants and those scheduled to go on-stream between 1978 and 1981 encompass a wide range of production capacities and feedstock combinations. Tables IV-1 and IV-2 provide breakdowns as to capacities and feedstocks by production plants.[1--3] Many plant sites have more than one ethylene unit. The total capacity shown (20,456 Gg/yr) and the total number of process units (67) include both those currently in operation and those projected to start up within the next 5 years. As a number of older units are expected to shut down during the period, the actual total capacity at any specific time will be somewhat less. As shown by Table IV-1, the most prevalent processes in terms of total production capacity and number of operating units include ethane/propane plants with ethylene capacities of 160 to 340 Gg/yr and naphtha and/or gas-oil plants with capacities of 340 to 610 Gg/yr. Most units expected to go on stream within the next 2 years will have naphtha/gas-oil flexibility and will be capable of producing at least 450 Gg of ethylene per year.

The following ten model plants will be considered based on 8760 hr of operation annually:

Model No.	Feed Composition	Ethylene Production Capacity* [Gg/yr (lb/yr)]
I	100% ethane	226.8 (500 X 10^6)
II	100% propane	226.8 (500 X 10^6)
III	50% ethane, 50% propane	226.8 (500 X 10^6)
IV	50% ethane, 50% propane	158.7 (350 X 10^6)
V	50% ethane, 50% propane	340.1 (750 X 10^6)
VI	100% naphtha	544.2 (1200 X 10^6)
VII	100% gas oil	544.2 (1200 X 10^6)
VIII	50% naphtha, 50% gas oil	544.2 (1200 X 10^6)
IX	50% naphtha, 50% gas oil	680.3 (1500 X 10^6)
X	50% naphtha, 50% gas oil	408.2 (900 X 10^6)

*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and the annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is gegligible.

Table IV-1. Capacity Data for Plants Using Various Feedstocks

Feedstock	Number of Plants	Ethylene Capacity (Gg/yr)		
		Plant	Total	Average
Ethane, propane, butane	5	<160	381	77
	30	160-340	6952	232
	4	>340	1753	438
Naphtha, gas oil, field condensate	2	<340	426	213
	14	340-610	7166	512
	2	>610	1451	726
Mixed gas liquid and heavy liquid	2	<340	526	263
	4	340-610	1723	431
	0	>610	0	0

Table IV-2. Ethylene Production from Various Feedstock Combinations

Feedstocks	Number of Plants	Total Ethylene Capacity (Gg/yr)
Ethane	3	521
Propane	1	159
Ethane, propane	25	5642
Ethane, propane, butane	5	1818
Refinery off-gas	3	50
Refinery off-gas, ethane, propane	5	839
Ethane, propane, naphtha	5	1841
Naphtha	4	1447
Naphtha, gas oil	8	4580
Gas oil	3	1950
Field condensate	1	340
Naphtha, field condensate, raffinate	2	680
Naphtha, ethane, propane, refinery off-gas	1	408
Butane	1	181
	67	20,456

Estimated emissions for Models VI through X (naphtha and/or gas oil) are based on the process shown in Fig. III-1 and described in Sect. III-B. Naphtha/gas-oil flexibility is assumed (i.e., process equipment and storage tanks for Models VI through VIII are the same and variations in emissions are caused by variations in feed composition only).

Emissions for Models I through V (ethane and/or propane) are based on the process shown in Fig. III-2, with storage tank capacities sized for specific feed composition.

For Model I (ethane feed) it was assumed that propylene, C_4 compounds, and pyrolysis gasoline are separated as co-products. This simplifying assumption permits emissions from processes using mixed ethane/propane feeds to be estimated for the entire range of ethane/propane ratios from the single-feed component models. Processes with ethane as the sole feed component and in which co-products are not separated are relatively few and account for only a small fraction of total ethylene production.

Criteria for process, storage, fugitive, and secondary emissions for the models are discussed in the corresponding emissions sections: process emissions, Sects. 2.a. and b.; fugitive emissions, Sect. 2.c; storage emissions, Sects. 2.d and e; and secondary emissions, Sect. 2.f. Atmospheric dispersion parameters for Model-Plants III and VIII are given in Appendix B.

2. Sources and Emissions

Benzene and VOC emission rates and ratios (emissions/ethylene production) for the ten models are summarized in Tables IV-3 through IV-7 and are shown graphically in Figs. IV-1 and IV-2. Estimated VOC emissions do not include methane (methane and hydrogen are significant components of intermittent and fugitive emissions).

Because intermittent emissions (Vent E) predominate and are significantly less with dual refrigeration and charge-gas compressor trains, estimates of intermittent emissions are included for both single- and dual-train processes.

a. Normal Process Emissions -- Process emissions of VOC and benzene occurring during normal operation are very low for all models. Characteristics of the emissions

Table IV-3. Benzene and Total VOC Uncontrolled Emissions for Model-Plants I and II

Source	Source Designation (Fig. III-2)	Emission Ratio[a] (g/Mg)		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
		Model-Plant I[b]			
Compressor lube-oil vents	G				
Single compressor trains		0.0348	13.9	0.0009	0.36
Dual compressor trains		0.0696	27.8	0.0018	0.72
Other normal process emissions	A,B,D,F		27.6		0.71
Intermittent emissions	E				
Single compressor trains		29.8	6910	0.77	179.0
Dual compressor trains		3.8	1506	0.099	39.0
Storage tanks	C	3.4	24	0.088	0.61
Salt-dome storage	H		274		7.1
Fugitive		8.3	3608	0.21	93.4
Secondary	K	8.9	23	0.23	0.59
		Model-Plant II[c]			
Compressor lube-oil vents	G				
Single compressor trains		0.187	13.9	0.00483	0.36
Dual compressor trains		0.374	27.8	0.00966	0.72
Other normal process emissions	A,B,D,F		51.5		1.33
Intermittent emissions	E				
Single compressor trains		235.8	8460	6.1	219.0
Dual compressor trains		30.1	1704	0.78	44.1
Storage tanks	C	27.7	195	0.71	5.0
Salt-dome storage	H		274		7.1
Fugitive		43.0	3295	1.11	85.3
Secondary	K	8.9	23	0.23	0.59

[a] g of benzene or total VOC per Mg of ethylene produced.

[b] Feed, ethane; ethylene capacity, 226.8 Gg/yr.

[c] Feed, propane; ethylene capacity, 226.8 Gg/yr.

Table IV-4. Benzene and Total VOC Uncontrolled Emissions for Model-Plants III and IV

Source	Source Designation (Fig. III-2)	Emission Ratio[a] (g/Mg)		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
		Model Plant III[b]			
Compressor lube-oil vents	G				
Single compressor trains		0.111	13.9	0.00288	0.36
Dual compressor trains		0.222	27.8	0.00576	0.72
Other normal process emissions	A,B,D,F		39.6		1.025
Intermittent emissions	E				
Single compressor trains		116.3	7822	3.0	202.5
Dual compressor trains		14.9	1621	0.39	42.0
Storage tanks	C	15.8	111	0.41	2.9
Salt-dome storage	H		274		7.1
Fugitive		25.6	3453	0.66	89.4
Secondary	K	8.9	23	0.23	0.59
		Model Plant IV[c]			
Compressor lube-oil vents	G				
Single compressor trains		0.159	19.9	0.00288	0.36
Dual compressor trains		0.318	39.7	0.00576	0.72
Other normal process emissions	A,B,D,F		39.6		0.72
Intermittent emissions	E				
Single compressor trains		116.3	7822	2.1	141.7
Dual compressor trains		14.9	1621	0.27	29.4
Storage tanks	C	15.9	112	0.29	2.0
Salt-dome storage	H		276		5.0
Fugitive		36.7	4935	0.66	89.4
Secondary	K	8.9	23	0.16	0.42

[a] g of benzene or total VOC per Mg of ethylene produced.

[b] Feed, 50% ethane-50% propane; ethylene capacity, 226.8 Gg/yr.

[c] Feed, 50% ethane-50% propane; ethylene capacity, 158.7 Gg/yr.

Table IV-5. Benzene and Total VOC Uncontrolled Emissions for Model-Plants V and VI

Source	Source Designation (Fig. III-2)	Emission Ratio[a] (g/Mg)		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
		Model Plant V[b]			
Compressor lube-oil vents	G				
Single compressor trains		0.0740	0.25	0.00288	0.36
Dual compressor trains		0.1480	18.50	0.00576	0.72
Other normal process emissions	A,B,D,F		39.6		1.54
Intermittent emissions	E				
Single compressor trains		116.4	7822	4.5	303.7
Dual compressor trains		14.9	1621	0.58	63.0
Storage tanks	C	15.6	110	0.61	4.3
Salt-dome storage	H		276		10.7
Fugitive		17.1	2303	0.66	89.4
Secondary	K	8.9	23	0.34	0.90
		Model Plant VI[c]			
Compressor lube-oil vents	G				
Single compressor trains		0.193	5.79	0.0120	0.36
Dual compressor trains		0.386	11.60	0.0240	0.72
Other normal process emissions	A,B,D,F		72.0		4.47
Intermittent emissions	E				
Single compressor trains		733.2	11,690	45.6	726.0
Dual compressor trains		93.6	2,114	5.8	131.3
Storage tanks	C	143.2	1,067	8.9	66.3
Salt-dome storage	H		274		17.0
Fugitive		44.5	1,450	2.8	90.1
Secondary	K	15.5	40	0.96	2.47

[a] g of benzene or total VOC per Mg of ethylene produced.

[b] Feed, 50% ethane-50% propane; ethylene capacity, 340.1 Gg/yr.

[c] Feed, naphtha; ethylene capacity, 544.2 Gg/yr.

Table IV-6. Benzene and Total VOC Uncontrolled Emissions for Model-Plants VII and VIII

Source	Source Designation (Fig. III-2)	Emission Ratio[a] (g/Mg)		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
		Model-Plant VII[b]			
Compressor lube-oil vents	G				
Single compressor trains		0.206	5.79	0.0128	0.36
Dual compressor trains		0.412	11.60	0.0256	0.72
Other normal process emissions	A,B,D,F		88.8		5.51
Intermittent emissions	E				
Single compressor trains		851.4	12,968	52.9	805.6
Dual compressor trains		108.7	2,278	6.8	141.5
Storage tanks	C	151.6	1,068	9.4	66.3
Salt-dome storage	H		274		17.0
Fugitive		47.4	1,466	2.9	91.1
Secondary	K	28.0	73	1.74	4.52
		Model-Plant VIII[c]			
Compressor lube-oil vents	G				
Single compressor trains		0.200	5.79	0.0124	0.36
Dual compressor trains		0.400	11.60	0.0248	0.72
Other normal process emissions	A,B,D,F		80.4		4.99
Intermittent emissions	E				
Single compressor trains		791.9	12,314	49.2	765.0
Dual compressor trains		101.1	2,195	6.3	136.3
Storage tanks	C	147	1,068	9.2	66.3
Salt-dome storage	H		274		17.0
Fugitive		45.9	1,460	2.85	90.7
Secondary	K	21.7	56	1.35	3.49

[a] g of benzene or total VOC per Mg of ethylene produced.

[b] Feed, gas oil; ethylene capacity, 544.2 Gg/yr.

[c] Feed, 50% naphtha-50% gas oil; ethylene capacity, 544.2 Gg/yr.

Table IV-7. Benzene and Total VOC Uncontrolled Emissions for Model-Plants IX and X

Source	Source Designation (Fig. III-2)	Emission Ratio[a] (g/Mg)		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
	Model-Plant IX[b]				
Compressor lube-oil vents	G				
Single compressor trains		0.160	4.64	0.0124	0.36
Dual compressor trains		0.320	9.28	0.0248	0.72
Other normal process emissions	A,B,D,F		80.4		6.24
Intermittent emissions	E				
Single compressor trains		791.9	12,314	61.5	956.2
Dual compressor trains		101.1	2,195	7.9	170.5
Storage tanks	C	145.8	1,055	11.3	82.0
Salt-dome storage	H		274		21.3
Fugitive		36.8	1,168	2.85	90.7
Secondary	K	21.7	56	1.69	4.36
	Model-Plant X[c]				
Compressor lube-oil vents	G				
Single compressor trains		0.266	7.73	0.0124	0.36
Dual compressor trains		0.532	15.46	0.0248	0.72
Other normal process emissions	A,B,D,F		80.4		3.75
Intermittent emissions	E				
Single compressor trains		791.9	12,313	36.9	573.7
Dual compressor trains		101.1	2,194	4.7	102.2
Storage tanks	C	148.5	1,076	6.9	50.1
Salt-dome storage	H		275		12.8
Fugitive		61.2	1,946	2.85	90.7
Secondary	K	21.7	56	1.01	2.61

[a] g of benzene or total VOC per Mg of ethylene produced.

[b] Feed, 50% naphtha-50% gas oil; ethylene capacity, 680.3 Gg/yr.

[c] Feed, 50% naphtha-50% gas oil; ethylene capacity, 408.2 Gg/yr.

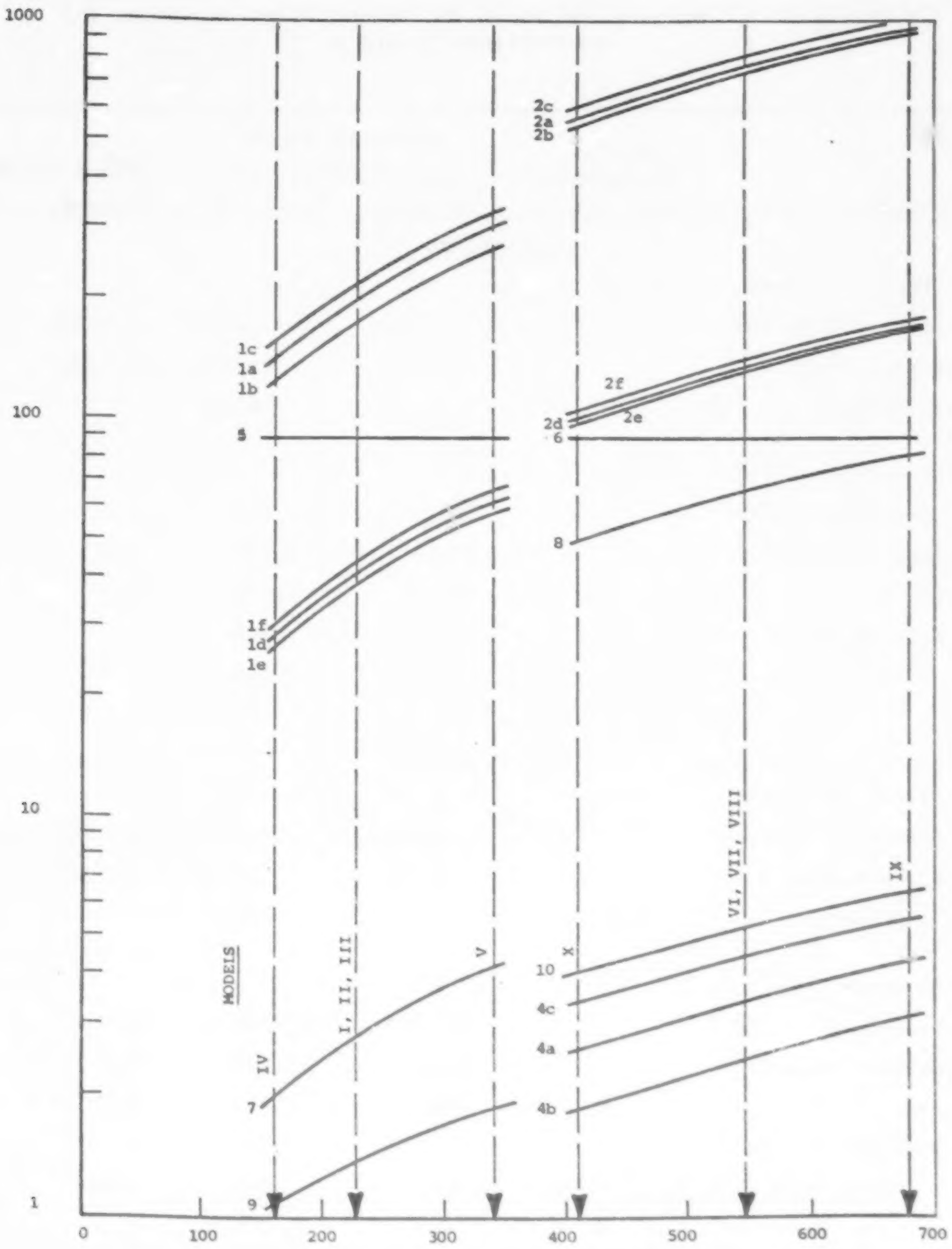

Fig. IV-1. Total Uncontrolled VOC Emissions vs Plant Capacity for Model Plants I Through X

Legend for Fig. IV-1.

Curve	Emission Source	Feedstock
1a	Intermittent (single compressor trains)	50:50 E/P
1b	Intermittent (single compressor trains)	Ethane
1c	Intermittent (single compressor trains)	Propane
1d	Intermittent (dual compressor trains)	50:50 E/P
1e	Intermittent (dual compressor trains)	Ethane
1f	Intermittent (dual compressor trains)	Propane
2a	Intermittent (single compressor trains)	50:50 N/G
2b	Intermittent (single compressor trains)	Naphtha
2c	Intermittent (single compressor trains)	Gas oil
2d	Intermittent (dual compressor trains)	50:50 N/G
2e	Intermittent (dual compressor trains)	Naphtha
2f	Intermittent (dual compressor trains)	Gas oil
3	Secondary emissions (below scale)	50:50 E/P
4a	Secondary emissions	50:50 N/G
4b	Secondary emissions	Naphtha
4c	Secondary emissions	Gas oil
5	Fugitive emissions	50:50 E/P
6	Fugitive emissions	50:50 N/G
7	Storage tanks	50:50 E/P
8	Storage tanks	50:50 N/G
9	Normal process emissions (single compressor trains)	50:50 E/P
10	Normal process emissions (single compressor trains)	50:50 N/G

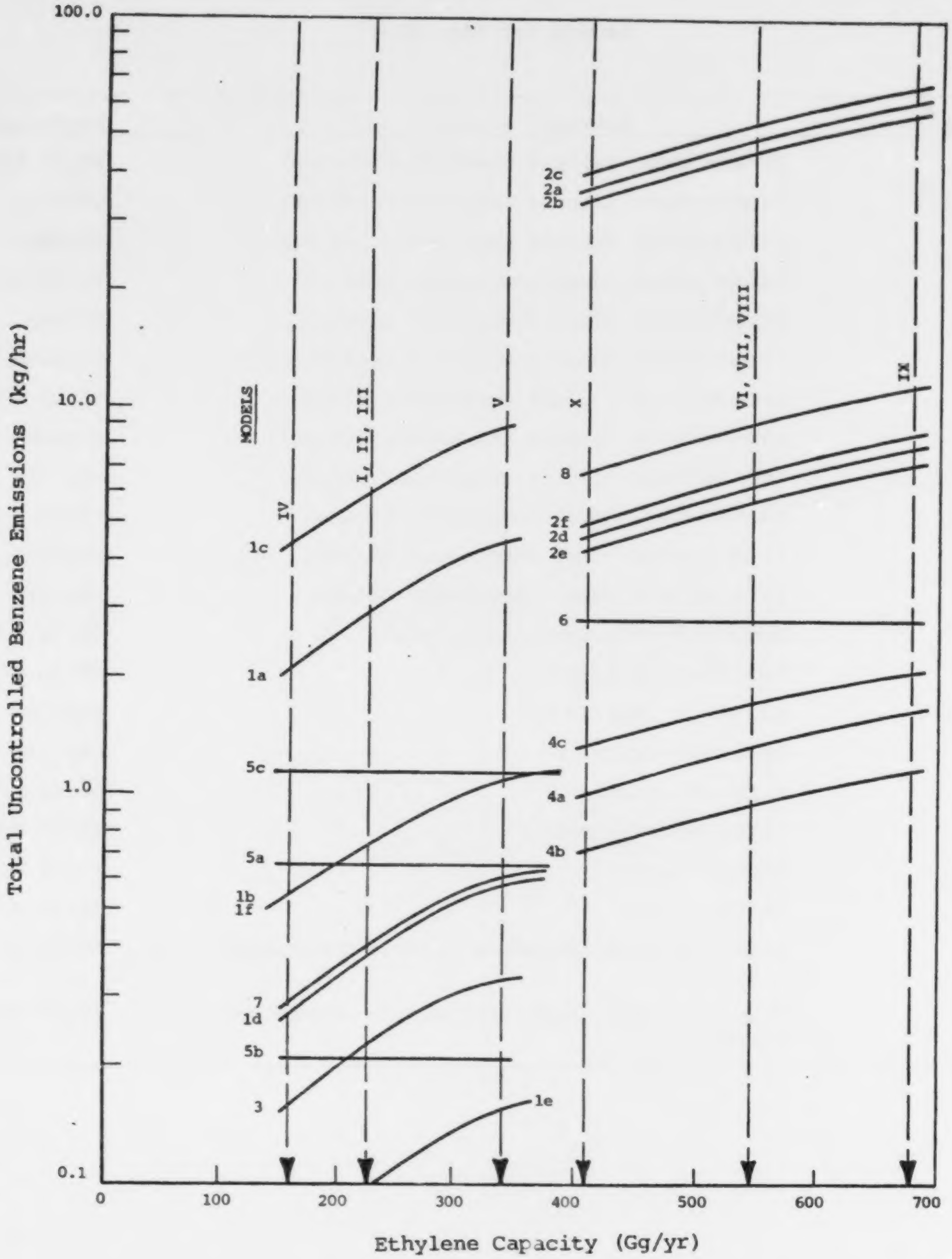

Fig. IV-2. Total Uncontrolled Benzene Emissions vs Plant Capacity for Model Plants I Through X

Legend for Fig. IV-2.

Curve	Emission Source	Feedstock
1a	Intermittent (single compressor train)	50:50 E/P
1b	Intermittent (single compressor train)	Ethane
1c	Intermittent (single compressor train)	Propane
1d	Intermittent (dual compressor trains)	50:50 E/P
1e	Intermittent (dual compressor train)	Ethane
1f	Intermittent (dual compressor train)	Propane
2a	Intermittent (single compressor train)	50:50 N/G
2b	Intermittent (single compressor train)	Naphtha
2c	Intermittent (single compressor train)	Gas oil
2d	Intermittent (dual compressor train)	50:50 N/G
2e	Intermittent (dual compressor train)	Naphtha
2f	Intermittent (dual compressor train)	Gas oil
3	Secondary emissions	50:50 E/P
4a	Secondary emissions	50:50 N/G
4b	Secondary emissions	Naphtha
4c	Secondary emissions	Gas oil
5a	Fugitive emissions	50:50 E/P
5b	Fugitive emissions	Ethane
5c	Fugitive emissions	Propane
6	Fugitive emissions	50:50 N/G
7	Storage tanks	50:50 E/P
8	Storage tanks	50:50 N/G

from the sources identified in Figs. III-1 and III-2 are summarized in the following items (i)--(v).

(i) Flue gas (Vent A) -- Emissions are composed of combustion products generated from the combustion of primarily gaseous fuels (primarily H_2 and CH_4) separated from the cracked gas. The naphtha and/or gas-oil feedstock processes (Models VI through X) also utilize fuel oil produced from the process. VOC concentrations are relatively low, with no significant benzene concentration.

(ii) Pyrolysis furnace decoking (Vent B) -- Emissions are composed primarily of air, steam, CO_2, CO, and particles of unburned carbon, with no significant concentrations of VOC or benzene. The primary purpose of emission control devices is for particulate control.

(iii) Acid gas removal (Vent D) -- Emissions are composed primarily of H_2S, SO_2, and CO_2. Emission controls either remove and recover H_2S as sulfur or convert H_2S to SO_2 before venting.

(iv) Hydrogenation catalyst regeneration (Vent F) -- Emissions are infrequent, occurring only during catalyst regeneration (4- to 6-month intervals). VOC emissions are very low, with no significant concentrations of benzene.

(v) Compressor lubricating oil vents (Vent G) -- Although VOC concentrations are significant, the flow rates are relatively low. The charge-gas-compressor lubricating oil vent (Stream 47) is the only normal process vent emitting benzene.

Estimated normal process VOC emissions for Models VI through X (naphtha and/or gas-oil feedstocks) were developed directly from data received from ethylene manufacturers.[4,5] Because the reported data were for processes using both naphtha and gas oil, the normal process emissions for Models VI through VIII were assumed to be identical; the actual differences are minor. Estimated VOC emissions for Models I through V (ethane and/or propane) were developed from the same data based on the following criteria:

(i) The quantity of flue gas vented is proportional to the total quantity of feedstocks consumed. Feedstock requirements and yield structures for Models I through V were based on the ethane and propane data in Table II-1.

(ii) VOC concentration in the flue gas is identical for all models.

(iii) Total VOC emissions from compressor lubricating oil vents are the same for all models.

Normal process emissions of benzene (charge-gas compressor lube-oil vent only) are based on the following criteria:

(i) Benzene concentrations in the charge-gas compressor lube-oil vents are the same as compressor inlet concentrations (see Table IV-8).

(ii) Compressor inlet concentrations of benzene are as follows (from Table IV-8):

Model	Feed Composition	Benzene Concentration (wt %)
I	Ethane	0.44
II	Propane	2.28
III-V	50:50 E/P	1.36
VI	Naphtha	5.66
VII	Gas oil	6.03
VIII-X	50:50 N/G	5.85

b. Intermittent Emissions (Vent E) -- Most process emissions from all ethylene model plants occur as intermittent emissions. Intermittent emissions result from the activation of pressure-relief devices, the depressurization and purging of equipment in preparation for maintenance, and the intentional venting of off-specification products generated during abnormal conditions. Most intermittent emissions are caused by compressor outages, which primarily result in the venting of pyrolysis gas (process compressor charge gas, Stream 19).

With the exception of emissions from demethanizer relief valves all intermittent emissions are vented through the main process vent (Vent E). The demethanizer relief valves, which release primarily hydrogen and methane, are vented sepa-

Table IV-8. Typical Charge-Gas Compositions and Rates for Plants Producing 453.5 Gg/yr (1 billion lb/yr) of Ethylene from Various Feedstocks

Feedstock	% of Feed Recycled	Total Pyrolysis Gas Rate from Furnaces (Gg/yr)	Compressor Charge-Gas (Gg/yr)	Charge Gas Composition (wt %)							
				Hydrogen and Methane	Ethylene	Propylene	Ethane and Propane	Total C_4's	Contained Butadiene	Pyrolysis Gasoline	Contained Benzene
Ethane	40.0	772.4	772.0	8.6	58.7	1.5	28.6	1.7	1.2	0.9	0.44
Propane	15.0	1185.2	1175.8	25.1	38.6	14.0	13.1	3.9	2.6	5.3	2.28
50:50 E/P	23.7	978.8	973.9	16.9	48.7	7.8	20.8	2.8	1.9	3.1	1.36
Naphtha	10.0	1583.1	1474.1	15.3	30.8	13.9	9.8	9.3	4.5	20.9	5.66
Atmospheric gas oil	10.0	1951.7	1605.6	13.2	28.1	16.8	11.1	10.6	5.2	20.2	6.03
50:50 N/G	10.0	1767.4	1539.9	14.3	29.4	15.4	10.4	10.0	4.8	20.6	5.85

rately. Estimates of intermittent emissions for the model plants are based on the following criteria:

(i) Emissions of process compressor charge gas (Streams 50--52) are based on the 5-year average material losses caused by compressor outages, shown in Table III-1.[6] Table III-1 was developed for a plant with naphtha--gas-oil flexibility, producing 453.5 Gg of ethylene per year. The quantity of charge-gas emissions for all models is assumed to be proportional to the quantity of feedstocks consumed less the fuel oil produced (Table II-1). Fuel oil initially present in the pyrolysis gas (N/G processes only) is separated before compression and is usually not vented when a compressor outage occurs. Because Table III-1 applies to a process with naphtha/gas-oil flexibility, average values for naphtha and gas oil from Table II-1 were assumed for all naphtha and/or gas-oil models (Models VI-X). Although ethylene production/feed ratios are generally lower for gas oil than for naphtha, charge-gas compressor inlet rates (after pyrolysis fuel oil removal) are approximately the same at the same ethylene production rates.

(ii) The assumed compositions and rates of charge gas and the corresponding compositions of charge-gas emissions for the model plants, based primarily on the feed requirements and product yield data presented in Table II-1 and on typical recycle ratios for the various feed materials, are given in Table IV-8.

(iii) Charge-gas emissions from Table III-1 account for 95% of total intermittent emissions occurring with single compressor train operation (Table III-1 conditions only). For the model plants charge-gas emissions are assumed to be proportional to the respective charge-gas production rates, and other intermittent emissions are assumed to be proportional to the respective ethylene production rates and to contain no significant quantities of hydrogen, methane, or benzene. Other intermittent emissions are the same for both single and dual trains for all models. (The methods for calculating intermittent emissions are detailed in the sample calculations in Appendix F.)

c. Fugitive Emissions -- Process pumps, valves, compressors, continuous process analyzers, and process samples are potential sources of fugitive emissions. The factors used to establish the emission rates for pumps, valves, and compressors are shown in Appendix C. The number of emission sources is based on the following data for a naphtha/gas-oil feedstock process:[6]

Type of Source	Number
Pumps	165
Compressors	8
Valves	4150
Relief valves	65
Process samples	100/day

(Notes: Emissions from refrigeration and charge-gas compressor lube-oil vents are included in normal process emissons; fugitive emissions from relief valves are vented through the main process vent and are controlled with intermittent process emissions.)

Estimated emissions for the ten model plants are based on the following criteria:

(i) Total fugitive emissions (including H_2 and CH_4) for all models are the same.

(ii) 50% of fugitive emissions contain 100% nonmethane VOC.

(iii) 50% of fugitive emissions contain 85% nonmethane VOC.

(iv) 50% of fugitive emissions contain no benzene.

(v) The average benzene concentrations for the remaining 50% fugitive emissions are as follows (from Table IV-8):

Model	Benzene Concentration (%)
I	0.44
II	2.28
III-V	1.36
VI	5.66
VII	6.03
VIII-X	5.85

(vi) The collection of process samples in sample containers results in fugitive emissions of 0.085 m^3/sample.

(vii) Sample flow rates to continuous process analyzers are 2.8 X 10^{-3} m^3/min for each stream sampled. Twenty streams are continuously sampled in all model plants.

d. Storage Tanks -- Naphtha and gas-oil feedstocks (Models VI through X only) pyrolysis gasoline, and pyrolysis fuel oil (Models VI through X only) are the only feedstocks or products stored in atmospheric storage tanks (see Table IV-9). Ethylene is stored in underground salt domes. Gas liquid feedstocks (Models I through V) and other products (i.e., propylene, C_4 compounds) are stored in pressurized storage tanks, with no significant emissions resulting. All storage tank emission sources are shown on the flow diagram in Fig. III-2 (Vent C). Equations from AP-42 were used for the emission calculations. However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing-loss equation overpredicts emissions.[7]

Storage tanks for naphtha and gas-oil feedstocks (Models VI through X only) are sized to provide a 3-day supply. Feedstocks are normally consumed at the same rates at which they are received by pipeline, with storage tanks providing surge capacity for short-term differences between receiving and consuming rates. Pyrolysis gasoline storage tanks for all models have a 14-day capacity, and pyrolysis fuel oil storage tank capacity (Models VI through X) is 3 days. These storage capacities are consistent with data received from ethylene manufacturers.[4,5] Tanks are sized to conform with the yield structures shown in Table II-1. To provide naphtha/gas-oil flexibility, tanks are sized for the feedstock composition requiring the greatest capacity.

e. Salt-Dome Storage (Vent H) -- Emissions may result from the venting of ethylene absorbed in salt brine, which is displaced from the salt domes as ethylene is placed in storage. The estimated maximum uncontrolled emissions resulting from salt-dome storage that are given in Tables IV-1 through IV-7 are based on the following criteria:

1. Emissions are proportional to throughput and are independent of the total amount of ethylene in storage.

Table IV-9. Atmospheric Storage Tank Conditions

Contents	No. of Tanks	Tank Size (m³) Model I	II	III	IV	V	VI-VIII	IX	X	Turnovers Per Year	Tank Level (% of Heigh
Naphtha/gas oil[a]	2						10,670	13,340	8,000	0[b]	Constant 80
Raw pyrolysis gasoline	1						20,920	26,150	15,690	0[b]	Constant 80
Treated pyrolysis gasoline	2						10,460	13,070	7,850	26	10-80%
Pyrolysis gasoline (models I—V)	1	283	1105	695	486	1043				26	10-80%
Light pyrolysis fuel oil[c]	1						1,139	1,424	854	0[b]	Constant 80
Heavy pyrolysis fuel oil[c]	1						2,152	2,690	1,614	0[b]	Constant 80

[a] Emissions from fixed-roof tanks containing gas oil were insignificant. Floating-roof-tank emissions were determined for naphtha only.

[b] These tanks provide surge capacity only.

[c] Emissions from fixed-roof tanks were insignificant; floating-roof-tank emissions were not determined.

2. The annual throughput for all models is equal to 15 days' production.[6]
3. The discharged brine is saturated with ethylene at the storage dome conditions.

Sample calculations are given in Appendix G.

The estimated emissions resulting from salt-dome storage, given in Tables IV-1 through IV-7, represent the maximum emissions that would occur from this source only if brine saturated with ethylene is discharged. Because only the brine adjacent to the ethylene-brine interface probably approaches saturation, the actual emissions are estimated to be much less if a substantial brine level is maintained at all times and if the brine is discharged from the bottom of the dome only.[8--10]

f. Secondary Emissions -- Secondary emissions of VOC and benzene can result primarily from the handling and disposal of process wastewater. For the model plants four potential secondary sources are indicated on the flow diagram, Fig. III-2 (Source K). The solid wastes from the process (coke, spent desiccant) do not present a significant emission potential. Coke, removed from the pyrolysis furnace coils and from transfer line exchangers, is primarily free carbon and polymer-like organics with very low vapor pressures. Desiccant replacement is infrequent (every 3 to 5 years), and most residual organics with significant vapor pressures are removed by steam purging before desiccant replacement. Solid-waste disposal is normally by landfill.

No actual plant data on emissions from process wastewater were available. For the model plants emission estimates are based on the criteria given in Table IV-10 (see refs. 11 and 12).

Actual VOC and benzene emissions from wastewater may vary significantly from the estimated emissions for the models. Additional plant and experimental data are needed for a more accurate assessment. Secondary emissions and controls for all areas of the synthetic organic chemical industry are covered in a separate report.[12]

Table IV-10. Wastewater Parameters

Model No. and Feed	Parameters: Wastewater/ Ethylene Ratio (m^3/Gg)[a]	Avg. Conc. of Organic Compounds[b] (ppm by wt)	Emission Ratio[c] (kg/kg)	Benzene Concentration in Emitted VOC[d] (%)
I--V, E/P	889	104	0.25	38.5
VI, naphtha	1528	104	0.25	38.5
VII, gas oil	2804	104	0.25	38.5
VIII--X, 50-50 N/G	2166	104	0.25	38.5

[a] m^3 of wastewater per Gg of ethylene product; see ref 11.

[b] See ref. 4.

[c] kg of VOC emitted per kg of organics in wastewater. Results of air stripping experiments (see ref 12) indicate that from 0 to 50% of contained organics are vented during transfer and biological treatment of wastewater, depending primarily on activity coefficient of organic components. An average value of 25% was assumed.

[d] Benzene concentration for all model plants is based on the composition of vapor vented from the quench water from an ethane/propane feedstock process.

B. OTHER PROCESSES

Emission data for the developmental processes described in Sect. III-D are not currently available.

C. REFERENCES*

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6. R. P. Paveletic, H. C. Skinner, and D. Stewart, "Why Dual Ethylene Unit Compressors?" Hydrocarbon Processing 55(10), 135--138 (1976).

7. E. C. Pulaski, TRW Inc., letter dated May 30, 1979, to Richard Burr, EPA.

8. J. P. Walsh, Exxon Chemical Co., letter dated Feb. 26, 1979, to EPA with information on ethylene process at Baton Rouge, LA, in response to EPA request for comments on ethylene draft report.

9. R. J. Feldman, C. E. Lummus Co., letter dated Mar. 22, 1979, to EPA responding to EPA request for comments on ethylene draft report.

10. C. A. Gosoline, MCA, letter dated Jan. 25, 1979, to EPA responding to EPA request for comments on ethylene draftreport.

11. A. D. Little, Inc., Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Volume VI. "Olefins Industry Report," PB 264 272 (EPA-600/7-76-034f), U.S. Dept. of Commerce (December 1976) (available from the National Technical Information Service, Springfield, VA).

12. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Secondary Emissions (June 1980) (EAP/ESED report, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. CURRENT PYROLYSIS PROCESSES

Estimates of total controlled VOC and benzene emission rates and ratios (emissions/ethylene production) for the ten model plants, with single and dual compressor trains and with various control options are summarized in Tables V-1* through V-10 and are shown graphically in Figs. V-1 and V-2.

1. Normal Process Emissions

The compressor lubricating-oil vents are relatively small sources of VOC and benzene emissions and no specific controls have been specified for the model plants. These emissions can be effectively controlled by being recycled to the charge-gas compressor suction; however, because of the relatively small quantities of emissions occurring, the cost of the required piping may not be justifiable.

No additional controls for normal process emissions are indicated.

2. Intermittent Emissions

Intermittent process emissions can be effectively controlled by flares. Because these emissions are relatively infrequent, of short-term duration, and occur at extremely high and variable rates, other control methods are not generally applicable. Estimates of controlled intermittent emissions are included for both single and dual compressor train processes. Dual compressor trains are considered a process variation. Retrofitting of processes with single compressor trains to dual trains is not considered to be feasible.

Elevated flares that utilize steam injection to provide smokeless emissions are specified for the model plants. Other types of flares, primarily ground flares, and other methods of improving combustion (e.g., air injection, water spray) are less commonly used in the ethylene industry.[1--4] One ethylene manufacturer[5] who uses a ground flare with water spray for this purpose indicates that it has significant advantages. Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. The

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*The internal-floating-roof tanks referred to in Tables V-1--V-10 consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

Table V-1. Benzene and Total VOC Controlled Emissions for Model-Plant I[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg)		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.0348	13.9	0.0009	0.36
Dual compressor trains				0.0696	27.8	0.0018	0.72
Other normal process emissions	A,B,D,F	None			27.6		0.71
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	0.6	138	0.015	3.6
At 90% flare efficiency[c]			90.0	3.0	691	0.077	17.9
Dual compressor trains							
At 98% flare efficiency[c]			98.0	0.08	30	0.002	0.8
At 90% flare efficiency[c]			90.0	0.38	151	0.010	3.9
Storage tanks	C	Floating-roof tanks	85.0	0.5	3.6	0.013	0.09
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.8	1.58	690	0.041	17.9
Secondary	K	None		8.9	23	0.23	0.59

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-2. Benzene and Total VOC Controlled Emissions for Model-Plant II[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg)		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.187	13.9	0.00483	0.36
Dual compressor trains				0.374	27.8	0.00966	0.72
Other normal process emissions	A,B,D,F	None			51.5		1.33
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	4.7	169	0.122	4.4
At 90% flare efficiency[c]			90.0	23.6	846	0.61	21.9
Dual compressor trains							
At 98% flare efficiency[c]			98.0	0.6	34	0.016	0.9
At 90% flare efficiency[c]			90.0	3.0	170	0.078	4.4
Storage tanks	C	Floating-roof tanks	85.0	4.2	29.3	0.107	0.75
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	8.2	630	0.213	16.3
Secondary	K	None		8.9	23	0.23	0.59

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-3. Benzene and Total VOC Controlled Emissions for Model-Plant III[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg)		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.111	13.9	0.00288	0.36
Dual compressor trains				0.222	27.8	0.00596	0.72
Other normal process emissions	A,B,D,F	None			39.6		1.025
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	2.3	156	0.06	4.1
At 90% flare efficiency[c]			90.0	11.6	782	0.30	20.3
Dual compressor trains							
At 98% flare efficiency[c]			98.0	0.30	32	0.008	0.8
At 90% flare efficiency[c]			90.0	1.5	162	0.039	4.2
Storage tanks	C	Floating-roof tanks	85.0	2.4	16.7	0.062	0.44
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	4.9	660	0.127	17.1
Secondary	K	None		8.9	23	0.23	0.59

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-4. Benzene and Total VOC Controlled Emissions for Model-Plant IV[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg)		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.159	19.0	0.00298	0.36
Dual compressor trains				0.318	39.7	0.00576	0.72
Other normal process emissions	A,B,D,F	None			39.6		0.72
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	2.3	156	0.04	2.8
At 90% flare efficiency[c]			90.0	11.6	782	0.21	14.2
Dual compressor trains							
At 98% flare efficiency[c]			98.0	0.30	32	0.005	0.6
At 90% flare efficiency[c]			90.0	1.5	162	0.027	2.9
Storage tanks	C	Floating-roof tanks	85.0	2.39	16.8	0.044	0.30
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	7.0	943	0.127	17.1
Secondary	K	None		8.9	23	0.16	0.42

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-5. Benzene and Total VOC Controlled Emissions for Model-Plant V[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg)		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.0740	9.25	0.00288	0.36
Dual compressor trains				0.1480	18.50	0.00576	0.72
Other normal process emissions	A,B,D,F	None			39.6		1.54
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	2.3	156	0.09	6.1
At 90% flare efficiency[c]			90.0	11.6	782	0.45	38.4
Dual compressor trains							
At 98% flare efficiency[c]			98.0	0.30	32	0.012	1.3
At 90% flare efficiency[c]			90.0	1.5	162	0.058	6.3
Storage tanks	C	Floating-roof tanks	85.0	2.34	16.5	0.092	0.65
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	3.3	440	0.127	17.1
Secondary	K	None		8.8	23	0.34	0.90

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-6. Benzene and Total VOC Controlled Emissions for Model-Plant VI[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg) Benzene	Emission Ratio[b] (g/Mg) Total VOC	Emission Rate (kg/hr) Benzene	Emission Rate (kg/hr) Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.193	5.79	0.0120	0.36
Dual compressor trains				0.386	11.60	0.0240	0.72
Other normal process emissions	A,B,D,F	None			72.0		4.47
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	14.7	234	0.91	14.5
At 90% flare efficiency[c]			90.0	73.3	1169	4.56	72.6
Dual compressor trains							
At 98% flare efficiency[c]			98.0	1.9	42	0.12	2.6
At 90% flare efficiency[c]			90.0	9.4	211	0.58	13.1
Storage tanks	C	Floating-roof tanks	85.0	21.5	160.0	1.34	9.9
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	8.5	277	0.53	17.2
Secondary	K	None		15.5	40	0.96	2.47

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-7. Benzene and Total VOC Controlled Emissions for Model-Plant VII[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg)		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.206	5.79	0.0128	0.36
Dual compressor trains				0.412	11.60	0.0256	0.72
Other normal process emissions	A,B,D,F	None			88.8		5.51
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	17.0	259	1.06	16.1
At 90% flare efficiency[c]			90.0	85.1	1297	5.29	80.6
Dual compressor trains							
At 98% flare efficiency[c]			98.0	2.2	46	0.14	2.8
At 90% flare efficiency[c]			90.0	10.9	228	0.68	14.2
Storage tanks	C	Floating-roof tanks	85.0	22.7	160	1.41	9.9
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	9.1	281	0.56	17.4
Secondary	K	None		28.0	73	1.74	4.52

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-8. Benzene and Total VOC Controlled Emissions for Model-Plant VIII[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg)		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.200	5.79	0.0124	0.36
Dual compressor trains				0.400	11.60	0.0248	0.72
Other normal process emissions	A,B,D,F	None			80.4		4.99
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	15.8	246	0.98	15.3
At 90% flare efficiency[c]			90.0	79.2	1231	4.92	76.5
Dual compressor trains							
At 98% flare efficiency[c]			98.0	3.0	44	0.13	2.7
At 90% flare efficiency[c]			90.0	10.1	220	0.63	13.6
Storage tanks	C	Floating-roof tanks	85.0	22.1	160.2	1.38	9.9
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	8.8	279	0.55	17.3
Secondary	K	None		21.7	56	1.35	3.49

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-9. Benzene and Total VOC Controlled Emissions for Model-Plant IX[a]

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg) Benzene	Emission Ratio[b] (g/Mg) Total VOC	Emission Rate (kg/hr) Benzene	Emission Rate (kg/hr) Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.160	4.64	0.0124	0.36
Dual compressor trains				0.320	9.28	0.0248	0.72
Other normal process emissions	A,B,D,F	None			80.4		6.24
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	15.8	246	1.2	19.1
At 90% flare efficiency[c]			90.0	79.2	1231	6.2	95.6
Dual compressor trains							
At 98% flare efficiency[c]			98.0	2.0	44	0.16	3.4
At 90% flare efficiency[c]			90.0	10.1	220	0.79	17.1
Storage tanks	C	Floating-roof tanks	85.0	21.9.	158	1.69	12.3
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	7.0	223	0.55	17.3
Secondary	K	None		21.7	56	1.69	4.36

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table V-10. Benzene and Total VOC Controlled Emissions for Model-Plant X_a

Source	Source Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	Emission Ratio[b] (g/Mg)		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Compressor lube-oil vents	G	None					
Single compressor trains				0.266	7.73	0.0124	0.36
Dual compressor trains				0.532	15.46	0.0248	0.72
Other normal process emissions	A,B,D,F	None			80.4		3.75
Intermittent process emissions	E	Flares					
Single compressor trains							
At 98% flare efficiency[c]			98.0	15.8	246	0.74	11.5
At 90% flare efficiency[c]			90.0	79.2	1231	3.69	57.4
Dual compressor trains							
At 98% flare efficiency[c]			98.0	2.0	44	0.09	2.0
At 90% flare efficiency[c]			90.0	10.1	219	0.47	10.2
Storage tanks	C	Floating-roof tanks	85.0	22.3	161	1.04	7.5
Salt-dome storage	H	Maintain adequate brine inventory	100.0		0		0
Fugitive		Detection and correction of leaks, mechanical seals	80.9	11.7	372	0.55	17.3
Secondary	K	None		21.7	56	1.01	2.61

[a] Feed, ethane; ethylene capacity, 226.7 Gg/yr.

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

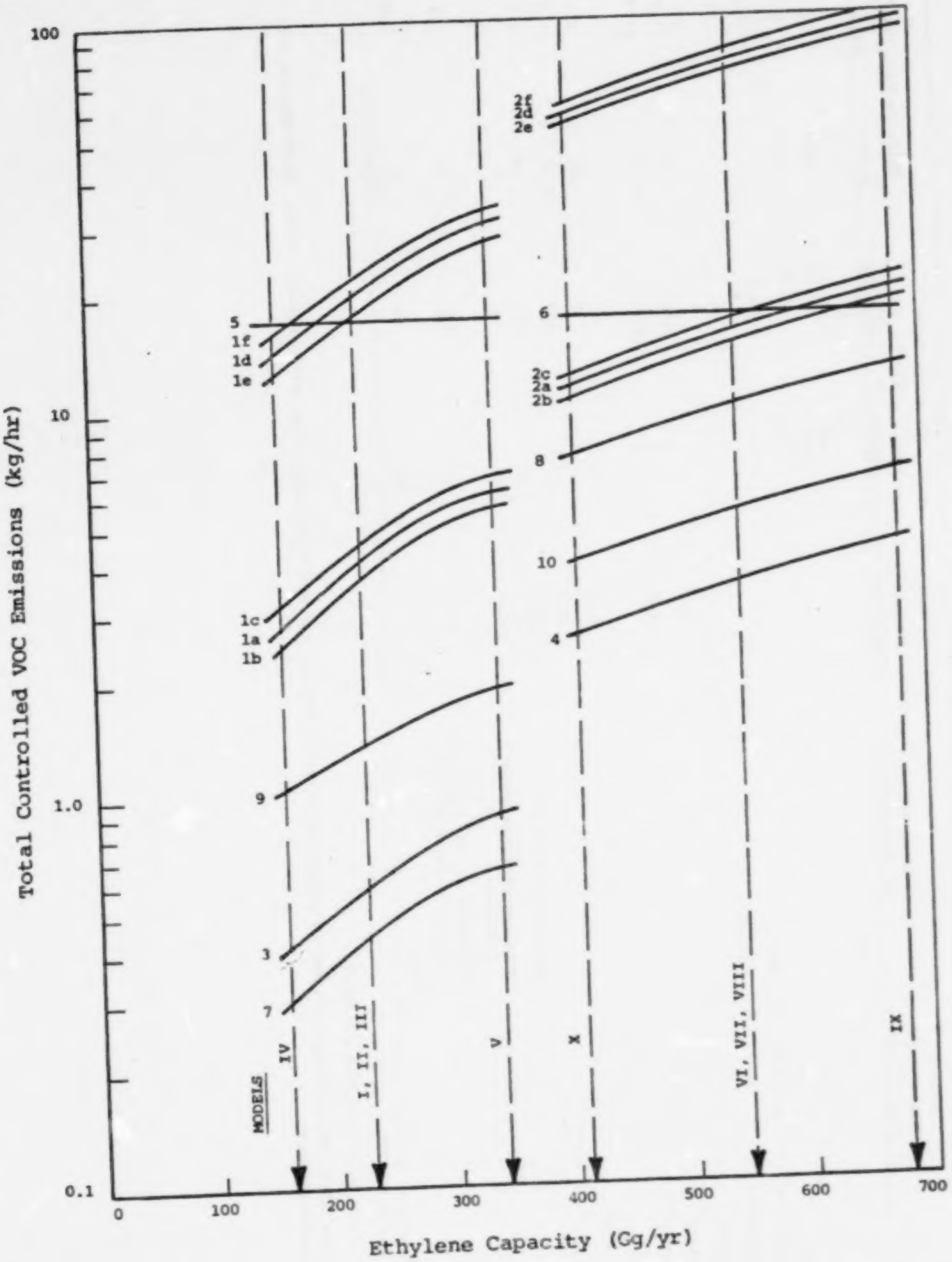

Fig. V-1. Total Controlled VOC Emissions vs Plant Capacity for Model Plants I Through X

Legend for Fig. V-1

Curve	Emission Source	Feedstock	Control Option
1a	Intermittent (single compressor trains)	50:50 E/P	Flare (98% removal)
1b	Intermittent (single compressor trains)	Ethane	Flare (98% removal)
1c	Intermittent (single compressor trains)	Propane	Flare (98% removal)
1d	Intermittent (single compressor trains)	50:50 E/P	Flare (90% removal)
1e	Intermittent (single compressor trains)	Ethane	Flare (90% removal)
1f	Intermittent (single compressor trains)	Propane	Flare (90% removal)
2a	Intermittent (single compressor trains)	50:50 N/G	Flare (98% removal)
2b	Intermittent (single compressor trains)	Naphtha	Flare (98% removal)
2c	Intermittent (single compressor trains)	Gas oil	Flare (98% removal)
2d	Intermittent (single compressor trains)	50:50 N/G	Flare (90% removal)
2e	Intermittent (single compressor trains)	Naphtha	Flare (90% removal)
2f	Intermittent (single compressor trains)	Gas oil	Flare (90% removal)
3	Secondary emissions	50:50 E/P	None
4	Secondary emissions	50:50 N/G	None
5	Fugitive emissions	50:50 E/P	Miscellaneous
6	Fugitive emissions	N/G (all ratios)	Miscellaneous
7	Storage tanks	50:50 E/P	Floating-roof tanks
8	Storage tanks	50:50 N/G	Floating-roof tanks
9	Normal process emissions (single compressor trains)	50:50 E/P	None
10	Normal process emissions (single compressor trains)	50:50 N/G	None

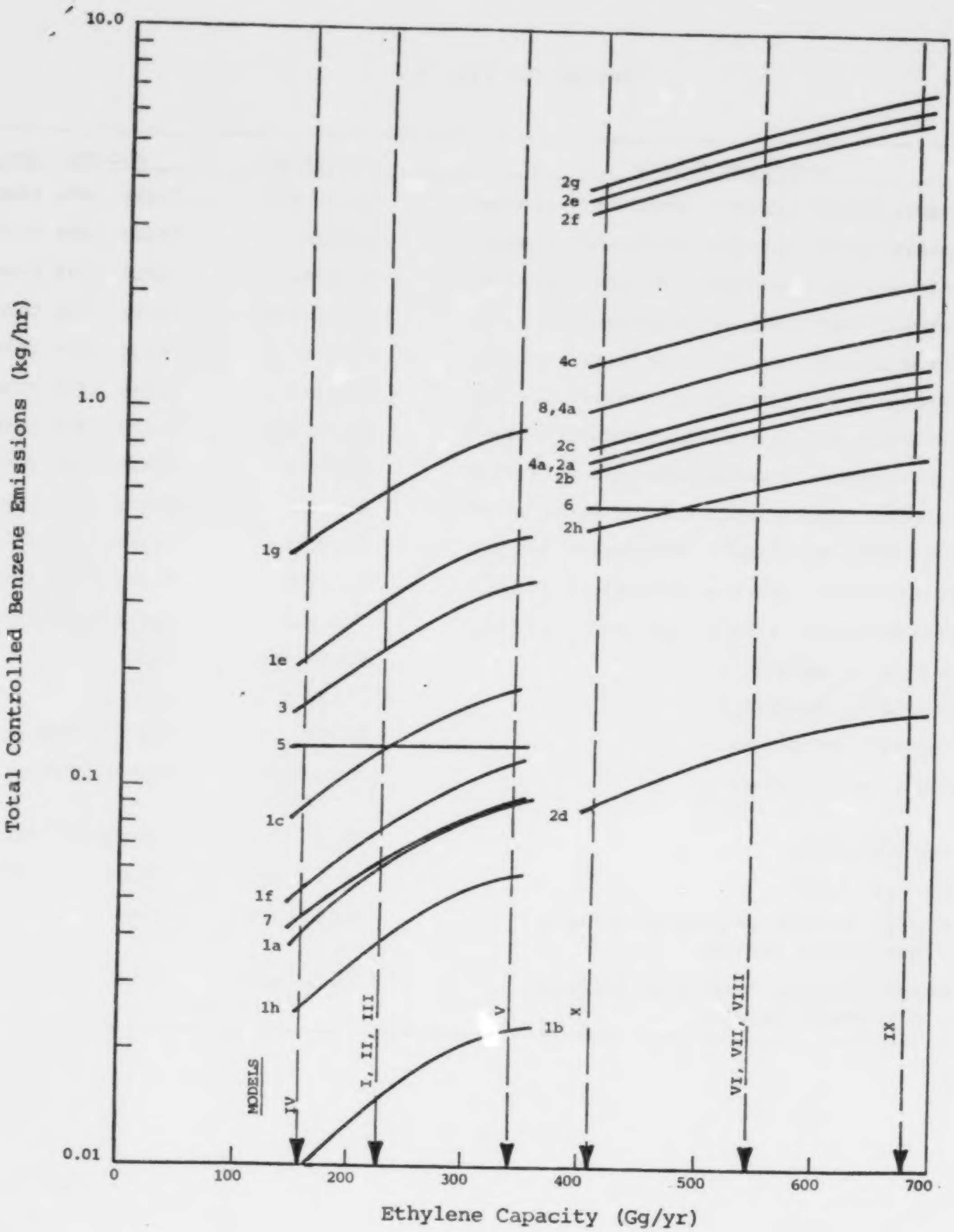

Fig. V-2. Total Controlled Benzene Emissions vs Plant Capacity for Model Plants I Through X

Legend for Fig. V-2.

Curve	Emission Source	Feedstock	Control Option
1a	Intermittent (single compressor trains)	50:50 E/P	Flare (98% efficiency)
1b	Intermittent (single compressor trains)	Ethane	Flare (98% efficiency)
1c	Intermittent (single compressor trains)	Propane	Flare (98% efficiency)
1d	Intermittent (dual compressor trains) (off scale)	50:50 E/P	Flare (98% efficiency)
1e	Intermittent (single compressor trains)	50:50 E/P	Flare (90% efficiency)
1f	Intermittent (single compressor trains)	Ethane	Flare (90% efficiency)
1g	Intermittent (single compressor trains)	Propane	Flare (90% efficiency)
1h	Intermittent (dual compressor trains)	50:50 E/P	Flare (90% efficiency)
2a	Intermittent (single compressor trains)	50:50 N/G	Flare (98% efficiency)
2b	Intermittent (single compressor trains)	Naphtha	Flare (98% efficiency)
2c	Intermittent (single compressor trains)	Gas oil	Flare (98% efficiency)
2d	Intermittent (dual compressor trains)	50:50 N/G	Flare (98% efficiency)
2e	Intermittent (single compressor trains)	50:50 N/G	Flare (90% efficiency)
2f	Intermittent (single comrpessor trains)	Naphtha	Flare (90% efficiency)
2g	Intermittent (single compressor trains)	Gas oil	Flare (90% efficiency)
2h	Intermittent (dual compressor trains)	50:50 N/G	Flare (90% efficiency)
3	Secondary emissions	50:50 E/P	None
4a	Secondary emissions	50:50 N/G	None
4b	Secondary emissions	Naphtha	None
4c	Secondary emissions	Gas oil	None
5	Fugitive emissions	50:50 E/P	Miscellaneous
6	Fugitive emissions	50:50 N/G	Miscellaneous
7	Storage tanks	50:50 E/P	Floating-roof tanks
8	Storage tanks	50:50 N/G	Floating-roof tanks
9	Normal process emissions (below scale)	50:50 E/P	None
10	Normal process emissions (below scale)	50:50 N/G	None

efficiencies used (90 and 98%) are for tentative comparison purposes. A detailed discussion of flares is presented in a separate EPA report.[6]

3. Fugitive Sources

Fugitive emissions and controls for the entire synthetic organic chemical industry are covered in a separate report.[7] Controlled fugitive emissions from valves, pumps, and compressors are based on the factors given in Appendix C and are included in Tables V-1 through V-10. These factors are based on the assumption that major leaks will be detected and repaired.

One ethylene manufacturer reports the use of tandem seals[2] (with the space between seals vented to pump suction) on all pumps in organic service to reduce fugitive losses. Data on the resulting reduction in emissions and the cost effectiveness are not currently available.

Emissions from process samples primarily result from purging of the sample lines and containers. Emissions can be effectively controlled by piping sample purge gas to the suction of the charge-gas compressor or to an existing combustion chamber. Continuous sample streams from process analyzers can be controlled with a similar collection system. A combined removal efficiency (process samples and continuous analyzers) of 95% is considered to be attainable.

4. Storage Tanks

Storage guidelines for all producers are discussed in a separate EPA report.[8] Control of storage losses with floating-roof tanks is considered for naphtha and pyrolysis gasoline only. Emissions from other materials stored at atmospheric pressure (i.e., gas oil, pyrolysis fuel oil) are extremely low and floating-roof tanks are not indicated. For processes with naphtha/gas-oil flexibility (Models VI--X), tanks primarily used for gas oil storage are equipped with floating roofs to permit alternate use for naphtha storage. Excluding ethylene storage (stored in salt domes) other feedstocks and products (i.e., gas liquid feedstocks, propylene, C_4 compounds) are stored in pressurized storage tanks, with no significant emissions.

Storage tank emissions listed in Tables V-1 through V-10 are based on the assumption that a contact type of internal floating roof* with secondary seals will reduce fixed-roof-tank emissions by 85%.[9,10]

5. Salt-Dome Storage

Emissions of ethylene vented from brine (displaced from the salt domes as ethylene is stored) are believed to be effectively controlled by maintaining a wide separation between the brine-ethylene interface and the brine discharge piping, with the brine being discharged from the bottom of the cavities.[11--14] Although no actual emission data are available, it is estimated that emissions are negligible if a "buffer zone" of at least 25—30 ft is maintained. An alternative control method would be to flare the vapor released by the discharged brine.

6. Secondary Emissions

Actual emissions from process wastewater may vary significantly from the emissions estimated for the model plants. The recycling of excess quench tower water as process steam (Stream 17), considered as a basic process feature in the flow sheets for the model plants, is an effective method of minimizing the quantity of quench water discharged. Specific data as to the concentrations of VOC and benzene in discharged quench water and in the blowdown from recycle steam generators are needed to estimate the reduction in VOC and benzene emissions that can be accomplished by recycling generated steam. No controls for secondary emissions are shown for the model plants.

B. OTHER PROCESSES

Data are not currently available for determination of the emission control requirements for the development processes described in Sect. III.D.

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*Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

C. REFERENCES*

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2. R. L. Standifer, IT Enviroscience, Trip Report for Gulf Oil Chemicals Co., Cedar Bayou Olefins Plant, Cedar Bayou, TX, Sept. 13-14, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. Responses to EPA request for information on emissions from ethylene manufacturers (see Appendix H).

4. Responses to EPA Questionnaires, Air Pollution Control and Cost Study of the Petrochemical Industry, OMB Approval No. 158 S 72019 (see Appendix H).

5. W. H. Lauderback, "Unique Flare System Retards Smoke," pp. 127, 128 Hydrocarbon Processing (January 1972).

6. V. Kalcevic, IT Enviroscience, Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED.) (Research Triangle Park, NC) (August 1980).

7. D. G. Erikson and V. Kalcevic, IT Enviroscience, Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC)

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9. C. C. Mosser, "Storage of Petroleum Liquids," Sect. 4.3 in Compilation of Air Pollutant Emission Factors, 3d ed., part A, AP-42, EPA (April 1977).

10. W. T. Moody, TRW Inc., letter dated Aug. 15, 1979, to D. A. Beck, EPA.

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13. C. A. Gosoline, CMA, letter dated Jan. 25, 1979, to EPA responding to EPA request for comments on ethylene draft report.

14. J. A. Mullins, Shell Oil Co., letter dated Jan. 3, 1979, to EPA responding to EPA request for comments on ethylene draft report.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

This section presents estimated costs and cost-effectiveness data for control of intermittent emissions of benzene and total VOC by the use of steam-assisted elevated flares. Details of the model plants are given in Sects. III and IV. The capital and annual costs presented for the process emission controls were obtained from the control device evaluation report for flares and the use of emissions as fuel.[1] The procedures used to develop the costs for the control systems are detailed in Appendix D.

Capital cost estimates represent the total investment required to purchase and install a complete flare system as defined in the control device evaluation report. Specific features of ethylene plant flare systems that are required because these systems must handle liquids and vapors released at low temperatures (e.g., vaporizers, additional knockout drums, materials suitable for low temperatures) may increase these costs significantly. These items are considered to be site-specific.

The bases for the annual cost estimates for the elevated flare systems include utilities, operating labor, maintenance supplies and labor, capital recovery charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. Annual costs are for a 1-year period beginning in December 1979. The cost factors used to compute annual costs are given in Table VI-1.

1. Current Pyrolysis Processes

a. Intermittent Emissions (Vent E)--Intermittent emissions, resulting from the activation of pressure relief devices, the depressurization and purging of equipment in preparation for maintenance, and the intentional venting of off-specification products generated during abnormal conditions, are controlled by elevated flares, with steam injection used to obtain smokeless emissions. Estimates of emission reductions, capital costs, total operating costs, and cost-effectiveness ratios for the ten model plants, with single and dual compressor trains, are summarized in Table VI-2. The relationships between

Table VI-1. Annual Cost Parameters

Operating factor	8760 hr/yr[a]
Operating labor	$15/man-hr
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital cost
Capital recovery, 18%[b]	
Taxes, insurances, administration charges, 5%	
Utilities	
Process water	$\$0.07/\mathrm{m}^3$ ($0.25/thousand gal)
Electric power	$8.33/GJ ($0.03/kWh)
Steam	$5.50/Mg ($2.50/thousand lb or million Btu)
Natural gas	$1.90/GJ ($2.00/thousand ft^3 or million Btu)
Heat recovery credits (equivalent to natural gas)	$1.90/GJ ($2.00/million Btu)

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[a] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[b] Based on 10-year life and 12% interest.

Table VI-2. Cost and Cost-Effectiveness Summary for Model-Plant Flares

Model Plant	Compressor Configuration	Maximum Smokeless Flaring Rate (M lb/hr)	Installed Capital Cost (M$)	Average VOC Discharge Rate (lb/hr)	Fuel Gas Cost (M$)	Fixed Cost (M$)	Steam Cost (M$)	Total Operating Cost (M$)	Cost Effectiveness at 98% Flare Efficiency ($/Mg of VOC)	Cost Effectiveness at 90% Flare Efficiency ($/Mg of VOC)	Cost Effectiveness at 98% Flare Efficiency ($/Mg of Benzene)	Cost Effectiveness at 90% Flare Efficiency ($/Mg of Benzene)
I	Single	46.9	175	395.0	3.8	50.8	2.6	57.2	37.2	40.5	8,638	9,405
I	Dual	46.9	175	86.0	3.8	50.7	0.6	55.1	164.6	179.2	64,830	70,594
II	Single	71.4	239	482.8	5.7	69.3	3.2	78.2	41.6	45.3	1,493	1,626
II	Dual	71.4	239	97.2	5.7	69.3	0.6	75.6	199.7	217.4	11,290	12,290
III	Single	59.1	201	446.4	4.4	58.2	2.9	65.5	37.7	41.0	2,543	2,769
III	Dual	59.1	201	92.6	4.4	58.2	0.6	63.2	175.3	190.9	18,880	20,550
IV	Single	41.4	154	312.4	3.3	44.7	2.1	50.1	41.2	44.8	2,779	3,026
IV	Dual	41.4	154	64.8	3.3	44.7	0.4	48.4	191.8	208.8	20,880	22,740
V	Single	88.7	282	669.5	7.2	81.9	6.6	95.7	36.7	40.0	2,477	2,697
V	Dual	88.7	282	138.9	7.2	81.9	1.4	90.5	167.3	182.2	18,180	19,790
VI	Single	214.7	572	1600.6	20.6	165.9	15.8	202.3	32.5	35.3	517	563
VI	Dual	214.7	572	289.5	20.6	165.9	2.9	189.4	168.0	183.0	3,804	4,142
VII	Single	233.9	617	1776.0	22.9	178.8	17.5	219.2	31.7	34.5	482.7	525.6
VII	Dual	233.9	617	312.0	22.9	178.8	3.1	204.8	168.6	183.6	3,508	3,820
VIII	Single	224.3	595	1686.5	21.8	172.5	16.6	210.9	32.1	35.0	499.3	543.7
VIII	Dual	224.3	595	300.5	21.8	172.5	3.0	197.3	168.6	183.6	3,648	3,972
IX	Single	280.4	731	2108.1	29.0	212.1	20.8	261.9	31.9	34.7	496.1	540.1
IX	Dual	280.4	731	375.9	29.0	212.1	3.7	244.8	167.2	182.1	3,610	3,930
X	Single	168.2	453	1264.8	14.5	131.4	12.5	158.4	32.2	35.0	500.0	544.5
X	Dual	168.2	453	225.3	14.5	131.4	2.2	148.1	168.8	183.8	3,671	3,997

production capacity and capital costs, total operating costs, and cost-effectiveness ratios are shown in Figs. VI-1 through VI-4.

Flare capital and operating costs for the specific models were obtained directly from the appropriate graphs and equations in the control device evaluation report on flares and the use of emissions as fuels.[1] The flare requirements for each model were based on the following criteria:

1. The flare is sized to smokelessly combust the maximum quantities of intermittent emissions vented during normal startup and shutdown operations. The maximum flare nonsmokeless capacity available for severe upset situations is much greater than the smokeless capacity. The relationship between smokeless capacity and maximum capacity at a pressure drop of 4.47 kPa (18 in. H_2O) is given in Fig. IV-1 of the cited control device evaluation report.[1]

2. The maximum quantity of intermittent emissions anticipated during normal startup and shutdown of a naphtha/gas-oil ethylene plant with a capacity of 589.7 Gg/yr (1300 million lb/yr) of ethylene is 110.2 Mg/hr (243,000 lb/hr).[2]

3. The maximum quantities of intermittent emissions anticipated for all model plants are proportional to the respective compressor charge-gas rates (see Table IV-8). Sample calculations of estimates of capital costs, operating costs, and cost-effectiveness ratios are given in Appendix D.

b. Normal Process Emissions--The compressor lubricating-oil vents (vent G) are the only normal process sources of benzene and VOC emissions for which controls were considered. (The control of SO_2, H_2S, and particulate emissions is not included in this report.) Emissions from the lubricating-oil vents can be effectively controlled by routing the vents to the charge-gas compressor suction. However, because the lubricating-oil vents are normally relatively minor sources of emissions and the cost of control is very site-specific, controls for the lubricating-oil vents are not specified for the model plants.

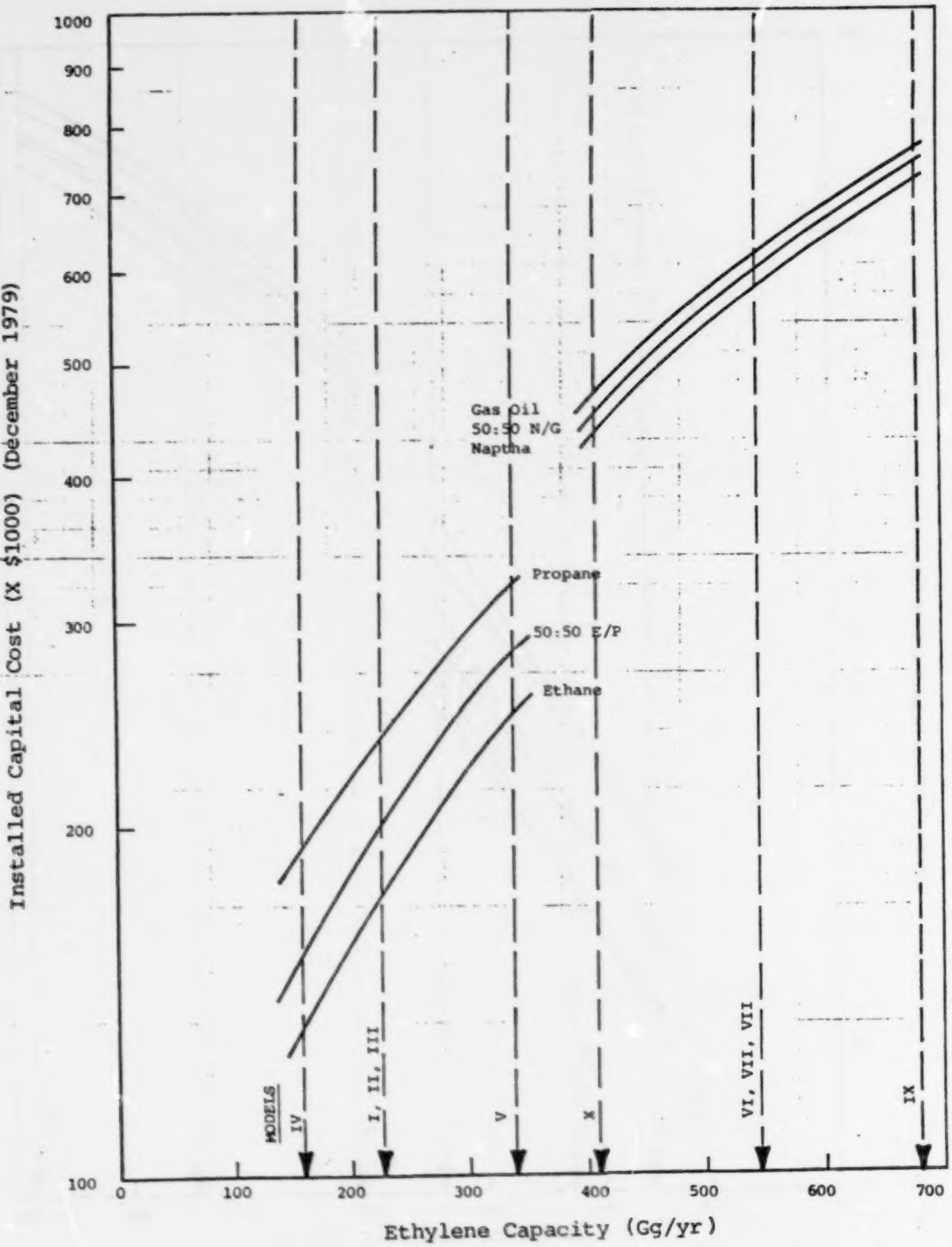

Fig. VI-1. Elevated Flare System Capital Costs

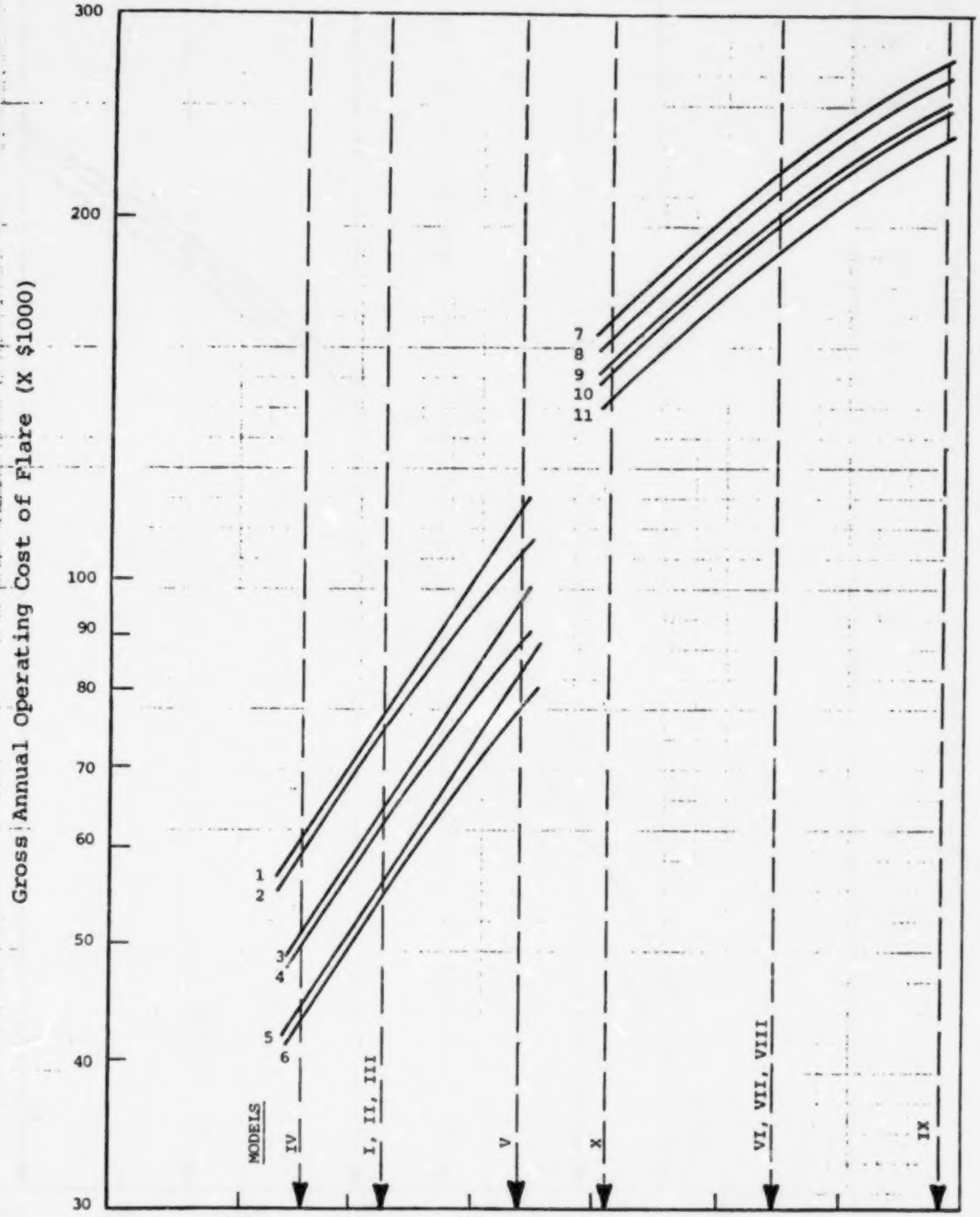

Fig. VI-2. Elevated-Flare-System Gross Annual Operating Cost

Legend for Fig. VI-2.

Curve	Feedstock	Process Configuration	Emission Source	Control
1	Propane	Single compressor trains	Intermittent	Flare
2	Propane	Dual compressor trains	Intermittent	Flare
3	50:50 E/P	Single compressor trains	Intermittent	Flare
4	50:50 E/P	Dual compressor trains	Intermittent	Flare
5	Ethane	Single compressor trains	Intermittent	Flare
6	Ethane	Dual compressor trains	Intermittent	Flare
7	Gas oil	Single compressor trains	Intermittent	Flare
8	50:50 N/G	Single compressor trains	Intermittent	Flare
9	50:50 N/G	Dual compressor trains	Intermittent	Flare
10	Naphtha	Single compressor trains	Intermittent	Flare
11	Naphtha	Dual compessor trains	Intermittent	Flare

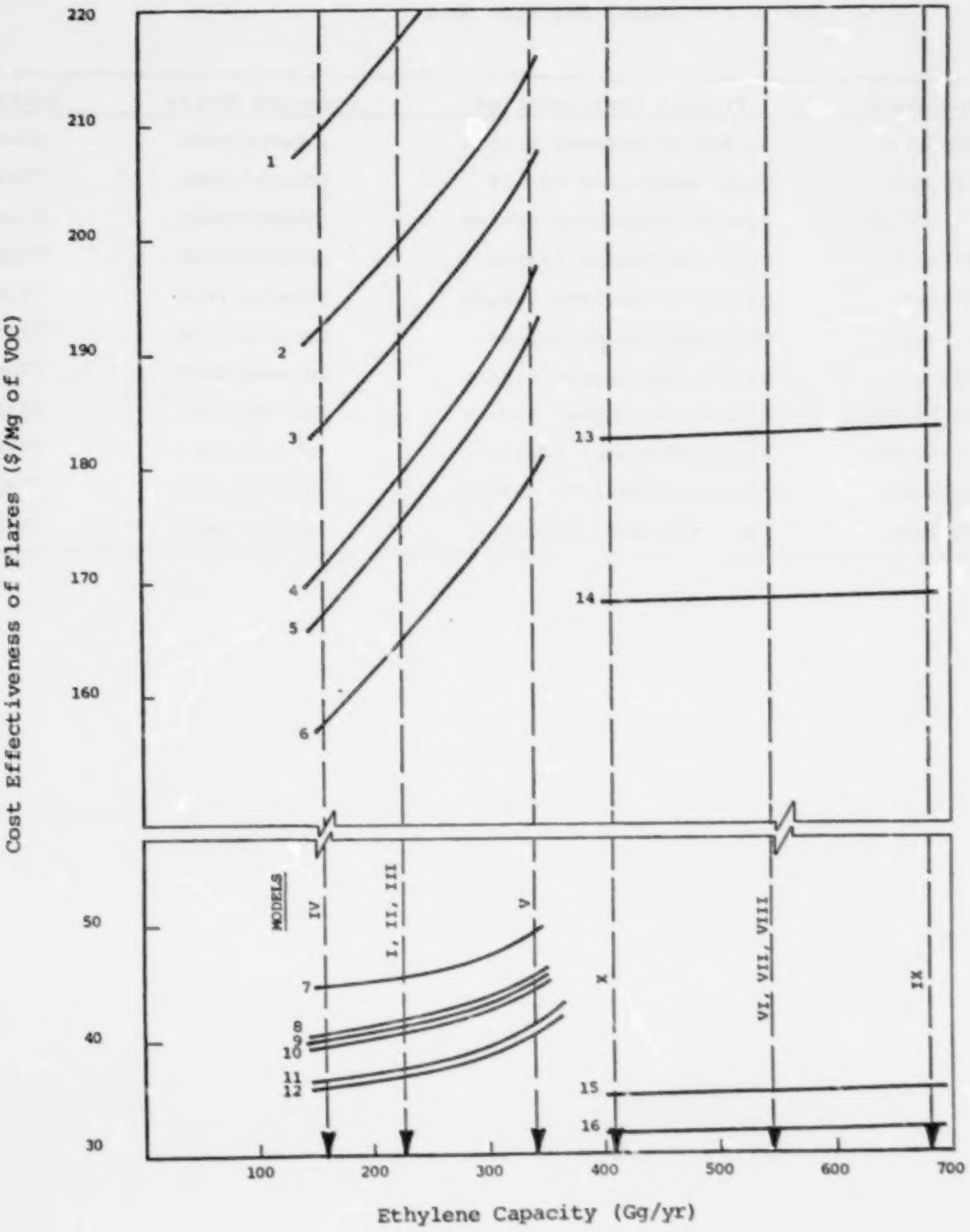

Fig. VI-3. Cost Effectiveness of Flares vs Plant Capacity for Control of Intermittent VOC Emissions from Model Plants I Through X

Legend for Fig. VI-3.

Curve	Feedstock	Compressor Trains	Flare Efficiency (%)
1	Propane	Dual	90
2	Propane	Dual	98
3	50:50 E/P	Dual	90
4	Ethane	Dual	90
5	50:50 E/P	Dual	98
6	Ethane	Dual	98
7	Propane	Single	90
8	Propane	Single	98
9	50:50 E/P	Single	90
10	Ethane	Single	90
11	50:50 E/P	Single	98
12	Ethane	Single	98
13	N/G (all ratios)	Dual	90
14	N/G (all ratios)	Dual	98
15	N/G (all ratios)	Single	90
16	N/G (all ratios)	Single	98

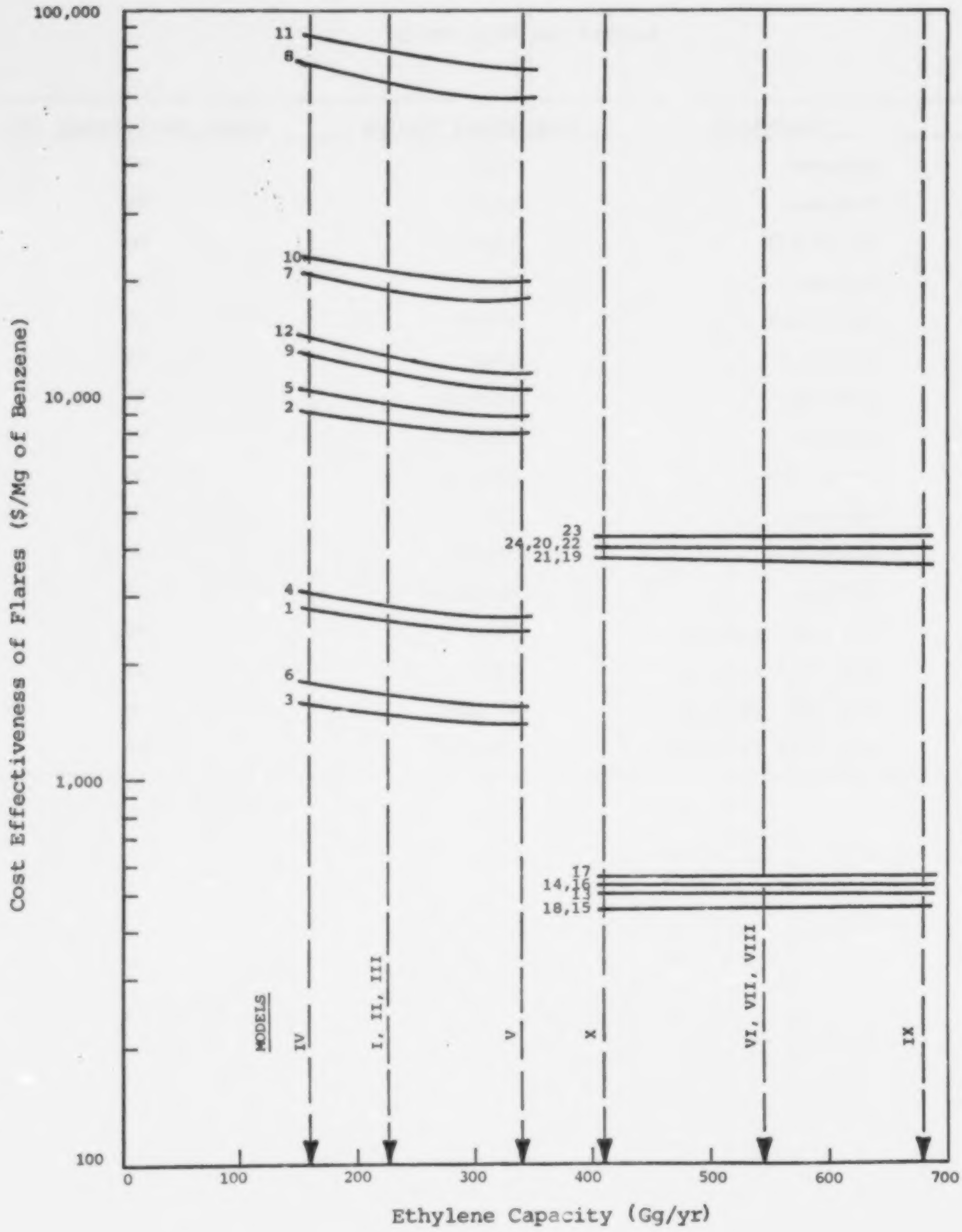

Fig. VI-4. Cost Effectiveness of Flares vs Plant Capacity for Control of Benzene Emissions from Model Plants I Through X

Legend for Fig. VI-4.

Curve	Feedstock	Compressor Trains	Flare Efficiency (%)
1	50:50 E/P	Single	98
2	Ethane	Single	98
3	Propane	Single	98
4	50:50 E/P	Single	90
5	Ethane	Single	90
6	Propane	Single	90
7	50:50 E/P	Dual	98
8	Ethane	Dual	98
9	Propane	Dual	98
10	50:50 E/P	Dual	90
11	Ethane	Dual	90
12	Propane	Dual	90
13	50:50 N/G	Single	98
14	Naphtha	Single	98
15	Gas oil	Single	98
16	50:50 N/G	Single	90
17	Naphtha	Single	90
18	Gas oil	Single	90
19	50:50 N/G	Dual	98
20	Naphtha	Dual	98
21	Gas oil	Dual	98
22	50:50 N/G	Dual	90
23	Naphtha	Dual	90
24	Gas oil	Dual	90

c. Storage Tank Emissions--Emissions of VOC and benzene from pyrolysis gasoline storage (all model plants) and emissions of VOC from naphtha storage (models VI—X only) are controlled by the use of floating-roof tanks. Installed capital cost, net annual cost, and cost-effectiveness data for retrofitting the Model-Plant fixed-roof tanks and the corresponding incremental costs of new internal-floating-roof tanks (based on the capital cost of new internal-floating-roof tanks minus capital cost of new fixed-roof tanks) are given in a separate EPA report.[3]

d. Salt-Dome Storage Emissions--Emissions of VOC, which occur when ethylene absorbed in brine is released, are controlled by maintaining a wide separation between the brine-ethylene interface and the brine discharge piping, thus preventing absorption of ethylene in the brine that is discharged. No specific costs are involved in this control technique.

e. Fugitive Sources--Control emission factors for fugitive sources are described in Appendix C. A separate EPA report covers fugitive emissions and their applicable controls for the synthetic organic chemicals manufacturing industry.[4] Capital requirements for controls for process samples and analyzer vents (see Sect. V-3) have not been determined. Cost estimates and cost-effectiveness ratios are not included.

f. Secondary Sources--No control systems are defined for secondary emissions from the model plants. Secondary sources and their controls are discussed in a separate EPA report.[5]

2. Other Processes

No data are available for determining the cost of any control devices required to control emissions from the alternative processes described in Sect. III-D.

B. ENVIRONMENTAL AND ENERGY IMPACTS

1. Current Pyrolysis Processes

Tables VI-3 and VI-4 show the environmental impacts of reducing benzene and VOC emissions by the application of the described control systems to Model-Plant III (50:50 E/P feed, 226.8-Gg/yr ethylene) and to Model-Plant VIII

Table VI-3. Environmental Impact of Controlled Model-Plant III (50:50 E/P Feed; 226.8-Gg/yr Ethylene) with Single and Dual Compressor Trains

Source	Stream Designation (Fig. III-3)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Mg/yr)	
				Benzene	Total VOC
Normal process emissions	A,B,D,F,G	None			
Intermittent process emissions	E	Elevated flare			
Single compressor trains			98[a]	25.8	1738
			90[a]	23.7	1596
Dual compressor trains			98[a]	3.3	361
			90[a]	3.1	331
Storage tanks	C	Internal floating roofs	85	3.0	21.5
Salt-dome storage	H	Maintain adequate brine inventory	100		62.1
Fugitive		Detection and correction of major leaks	81	4.7	633
Secondary	K	None			
Total with single compressor trains and 98% flare efficiency				33.5	2455
Total with single compressor trains and 90% flare efficiency				31.4	2313
Total with dual compressor trains and 98% flare efficiency				11.0	1078
Total with dual compressor trains and 90% flare efficiency				10.8	1047

[a] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

Table VI-4. Environmental Impact of Controlled Model-Plant VIII (50:50 N/G Feed; 544.2-Gg/yr Ethylene) with Single and Dual Compressor Trains

Source	Stream Designation (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Mg/yr) Benzene	Emission Reduction (Mg/yr) Total VOC
Normal process emissions	A,B,D,F,G	None			
Intermittent process emissions	E	Elevated flare			
Single compressor trains			98[a]	455	6923
			90[a]	420	6387
Dual compressor trains			98[a]	58.4	1216
			90[a]	54.0	1120
Storage tanks	C	Internal floating-roofs	85	70.3	494
Salt-dome storage	H	Maintain adequate brine inventory	100		149
Fugitive		Detection and correction of major leaks	81	20.6	646
Secondary	K	None			
Total with single compressor trains and 98% flare efficiency				546	8212
Total with single compressor trains and 90% flare efficiency				511	7676
Total with dual compressor trains and 98% flare efficiency				149	2505
Total with dual compressor trains and 90% flare efficiency				145	2409

[a] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

(50:50 N/G feed, 544.2-Gg/yr ethylene) with both single and dual compressor trains. Comparable information for other combinations of plant capacities, feedstocks, and process variations can be determined from the information presented in previous sections and from the appendices. Total energy consumption for a typical ethylene plant (excluding fuel value of products) is about 40 MJ per kg of ethylene produced.[6]

a. Elevated Flare System--Because flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels, the environmental impacts of flare systems with efficiencies of both 98% and 90% are included for tentative comparison purposes. With a flare efficiency of 98%, intermittent emissions of VOC from Model-Plant III are reduced by 1738 Mg/yr from plants with single compressor trains and by 361 Mg/yr from plants with dual compressor trains, with corresponding reductions in benzene emissions of 25.8 Mg/yr and 3.3 Mg/yr respectively. At a flare efficiency of 90%, VOC emissions are reduced by 1596 Mg/yr with single compressor trains and by 331 Mg/yr with dual trains. The corresponding reductions in benzene emissions are 23.7 Mg/yr and 3.1 Mg/yr, respectively.

The flare system energy requirements for Model-Plant III with single compressor trains are 3570 GJ/yr, which includes steam usage and the fuel gas required for the pilots and for purging.

At a flare efficiency of 98%, intermittent emissions of VOC from Model-Plant VIII are reduced by 6923 Mg/yr with single compressor trains and by 1216 Mg/yr with dual trains. The corresponding reductions in benzene emissions are 455 Mg/yr and 58.4 Mg/yr, respectively. With a flare efficiency of 90%, VOC emissions are reduced by 6387 Mg/yr with single compressor trains and by 1120 Mg/yr with dual trains. The corresponding reductions in benzene emissions are 420 Mg/yr and 54.0 Mg/yr, respectively. Energy requirements for the flare system for Model-Plant VIII with single compressor trains are 18,500 GJ/yr.

b. Controls for Other Emission Sources (Storage Tanks, Salt-Dome Storage, Fugitive) Control methods for these sources are floating-roof storage tanks, leak corrections for fugitive sources, and maintenance of adequate brine levels for salt-dome storage emissions. Application of these systems or methods result in VOC emission reductions of 717 Mg/yr and benzene emission reductions of 7.7 Mg/yr for Model-Plant III; in Model-Plant VIII the VOC emission reduction is 1289 Mg/yr and the benzene emission reduction is 91 Mg/yr. These control methods do not consume energy and have no adverse environmental or energy impacts.

No additional controls are proposed for secondary emissions.

2. Other Processes

Emission control systems for the developmental processes described in Sect. III-D have not been described.

C. REFERENCES*

1. V. Kalcevic, IT Enviroscience, Control Device Evaluation Flares and the Use of Emissions as Fuels (in preparation for EPA/ESED, Reasearch Triangle Park, NC).

2. R. L. Standifer, IT Enviroscience, Trip Report for Arco Chemical Company, Channelview, TX, Aug. 16-17, 1977 (on file at EPA/ESED, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Ethylene is produced in the United States predominately by the pyrolysis of natural-gas concentrates and refinery off-gas (primarily ethane and propane) and by the pyrolysis of petroleum liquids (primarily naphthas and atmospheric gas oils). Although ethylene produced from natural-gas concentrates and refinery off-gas accounted for about 70% of total ethylene in 1976 and production from these feedstocks is not expected to decrease significantly before 1982, almost all new capacity after 1979 will use the heavier petroleum liquid feedstocks.

The annual growth rate in ethylene production is estimated to be 4 to 4.5% through 1984; however, the development of new-production capacity is expected to stay well ahead of demand, with projected production at only 75% of capacity by 1981.[1]

Emission sources and control levels for Model-Plant III (feed, 50:50 ethane-propane; ethylene capacity, 226.8 Gg/yr) and Model-Plant VIII (feed, 50:50 naphtha--gas oil; ethylene capacity, 544.2 Gg/yr) are summarized in Tables VII-1 and VII-2 and are based on the use of single compressor trains with elevated flare systems controlling intermittent process emissions.

Table VII-3 gives a composite emission summary for all models based on the weighted averages of emissions from individual models. Emissions from individual models were weighted according to estimates of the actual industry distribution of feedstocks and process configurations. Because flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions, using specific fuels, emission estimates based on flare efficiencies of both 98% and 90% are included for tentative comparison purposes.

The current emissions projected for the domestic ethylene industry based on the estimated degree of control existing in 1980, with an average flare efficiency of 98%, are 1170 Mg/yr for benzene and 29,200 Mg/yr for total VOC. With an average flare efficiency of 90% the corresponding emissions are 1500 Mg/yr for

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[1] S. A. Cogswell, A. C. Gaessler, and T. A. Gibson, "CEH Marketing Research Report on Ethylene," pp. 300.5200H--300.5205I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1980).

Table VII-1. Emission Summary for Model-Plant III
(Feed, 50:50 E/P; Ethylene Capacity, 226.8 Gg/yr) with Single Compressor Trains

	Emission Rate (kg/hr)			
	Uncontrolled		Controlled	
Emission Source	Benzene	VOC	Benzene	VOC
Normal process emissions	0.0029	1.4	0.0029	1.4
Intermittent process emissions				
Flare efficiency 98%	3.0	202.5	0.06	4.1
Flare efficiency 90%	3.0	202.5	0.30	20.3
Storage and handling	0.41	10.0	0.06	0.44
Fugitive	0.66	89.4	0.13	17.1
Secondary	0.23	0.6	0.23	0.6
Total - 98% flare efficiency	4.3	303.9	0.48	23.6
Total - 90% flare efficiency	4.3	303.9	0.72	39.8

Table VII-2. Emission Summary for Model-Plant VIII
(Feed, 50:50 N/G; Ethylene Capacity, 544.2 Gg/yr) with Single Compressor Trains

	Emission Rate (kg/hr)			
	Uncontrolled		Controlled	
Emission Source	Benzene	VOC	Benzene	VOC
Normal process emissions	0.0124	5.4	0.0124	5.4
Intermittent process emissions				
Flare efficiency 98%	49.2	765.0	0.98	15.3
Flare efficiency 90%	49.2	765.0	4.92	76.5
Storage and handling	9.2	83.2	1.38	9.9
Fugitive	2.9	90.7	0.55	17.3
Secondary	1.4	3.5	1.35	3.5
Total - 98% flare efficiency	62.7	942.4	4.3	51.4
Total - 90% flare efficiency	62.7	942.4	8.2	112.6

Table VII-3. Composite Model-Plant Emission Summary[a]

	Emission Ratio (g/Mg)[b]			
	Uncontrolled		Controlled	
Emission Source	Benzene	VOC	Benzene	VOC
Normal process emissions	0.2	69	0.2	69
Intermittent emissions	325.9	7,247	6.5[c] 32.6[d]	145[c] 725[d]
Storage	66.4	755	10.0	72
Fugitive	31.3	2,677	6.0	572
Secondary	14.0	36	14.0	36
Total	437.8	10,784	36.7[c] 62.8[d]	834[c] 1414[d]

[a] Based on the weighted averages of the emissions from individual model plants. Emissions from individual models were weighted according to the following criteria (estimated to approximate actual industry distribution):

Feedstock distribution

Ethane/propane: 60% (37% ethane, 23% propane)

Naphtha/gas oil: 40%

Distribution of compressor configurations

E/P processes: 50% with single trains, 50% with dual or multiple trains

N/G processes: 90% with single trains, 10% with dual or multiple trains

[b] g of benzene or total VOC per Mg of ethylene produced.

[c] With a flare efficiency of 98%.

[d] With a flare efficiency of 90%.

benzene and 36,400 Mg/yr for total VOC. These emission estimates are based on engineering judgment and data from individual ethylene producers, state emission control agencies, and the open literature. Individual estimated projections are shown in Table VII-4.

The predominant emission sources are intermittent process emissions and fugitive emissions from both the gas-concentrate and petroleum-liquid feedstock processes and storage tank emissions from petroleum-liquid feedstock processes.

Intermittent process emissions can be effectively controlled by flares. Because these emissions are relatively infrequent, are of short-term duration, and occur at extremely high and variable rates, other control methods are not generally applicable. The installed cost of a steam-assisted elevated flare system for Model-Plant III is $200,000 and is $595,000 for Model-Plant VIII, based on information on general flare costs presented in a separate EPA report.[2] Specific features of ethylene plant flare systems may increase these costs significantly.

The corresponding cost-effectiveness ratios of steam-assisted elevated flare systems for Model-Plants III and VIII, with single and dual compressor trains and with flare efficiencies of 98% and 90%, are summarized in Table VII-5.

Emissions of benzene and VOC from atmospheric storage tanks can be effectively controlled by using internal-floating-roof tanks. The emission reduction would be 85%. Emissions resulting from the displacement of brine from salt-dome storage can be controlled by maintaining adequate separation of the ethylene-brine interface from the brine inlet line.

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[2] V. Kalcevic, IT Enviroscience, Control Device Evaluation. Flares and the Use Of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

Table VII-4. Estimated Emissions for the Industry

Source	1980 Emissions (Mg/yr)	
	Benzene	Total VOC
Normal process	2	960
Intermittent (98% flare efficiency)	530	11,800
Intermittent (90% flare efficiency)	855	19,000
Storage	294	2,880
Fugitive	153	13,040
Secondary	194	500
Total (98% flare efficiency)	1173	29,180
Total (90% flare efficiency)	1498	36,380

Table VII-5. Cost Effectiveness Ratios for Model-Plants III and VIII

Model Plant	Compressor Configuration	Flare Efficiency (%)	Cost Effectiveness ($/Mg)	
			Benzene	Total VOC
III	Single trains	98	2,540	38
III	Single trains	90	2,770	41
III	Dual trains	98	18,900	175
III	Dual trains	90	20,600	191
VIII	Single trains	98	500	32
VIII	Single trains	90	540	35
VIII	Dual trains	98	3,650	169
VIII	Dual trains	90	3,970	184

APPENDIX A

Table A-1. Physical Properties of Feedstocks and Products[a]

	Molecular Formula	Molecular Weight	Liquid Density[a]	Vapor Sp. Grav.	Boiling Point (°C)	Vapor Pressure
Feedstocks						
Ethane	C_2H_6	30.07	0.546 at -88°C	1.049	-88.6	
Propane	C_3H_8	44.09	0.585 at -44.5°C	1.562	-42.1	
n-Butane	C_4H_{10}	58.12	0.579 at 20°C		-0.5	
Naphtha[b]			0.694 at 35°C		91[c,d]	53.8 kPa at 35°C[e]
Gas oil[b]			0.873 at 35°C		320	3.03 Pa at 35°C[e]
Products						
Ethylene	C_2H_4	28.05	0.566 at -102°C	0.975	-103.7	
Propylene	C_3H_6	42.08	0.609 at -47°C	1.498	-47.7	
Butadiene	C_4H_6	54.09	0.621 at 20°C		-4.4	
Pyrolysis gasoline[b]			0.804 at 41°C		43[c,d]	58.6 kPa at 41°C[e]
Light fuel oil[b]			0.972 at 54°C		205[c,d]	80.0 Pa at 54°C[e]
Heavy fuel oil[b]			1.01 at 74°C		278[c,d]	65.5 Pa at 74°C[e]

[a] Unless otherwise noted, all values are from N. A. Lange, "Physical Properties of Organic Compounds," pp. 366--703 in Handbook of Chemistry, 8th ed., Handbook Publishers, Sandusky, OH, 1952.

[b] Properties of these materials vary. Values shown are typical examples.

[c] Initial boiling point.

[d] R. L. Standifer, IT Enviroscience, Inc., Trip Report for Arco Chemical Co., Channelview, Texas, August 16, 17, 1977 (on file at EPA/ESED, Research Triangle Park, NC).

[e] R. L. Standifer, IT Enviroscience, Inc., Trip Report for Gulf Oil Chemicals Co., Cedar Bayou Olefins Plant, Cedar Bayou, Texas, Sept. 13, 14, 1977 (on file at EPA/ESED, Research Triangle Park, NC).

APPENDIX B

Table B-1. Air-Dispersion Parameters for Model-Plant III (226.8-Gg/yr Ethylene, 50:50 Ethane/Propane Feed), Single Compressor Trains

Source	No. of Units	Emission Rate (g/sec) VOC	Emission Rate (g/sec) Benzene	Height (m)	Dia. (m)	Discharge Temp. (°C)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Ethane/propane pyrolysis furnace flue gas	6	0.02		27.5	1.0	170	12.3	15
Catalyst regeneration heater flue gas	1	0.004		15.2	0.4	704	1.7	15
Catalyst regeneration off-gas -- acetylene conv.	1			18.3	0.4	510	7.0	60
Compressor lube-oil vents (uncontrolled)								
Charge gas	1	0.05	0.0008	18.3	0.3	60		
Propylene	1	0.075		18.3	0.3	60		
Ethylene	1	0.075		18.3	0.3	60		
Main vent (uncontrolled)	1	56	0.8	76.2	0.73	38	64 (max)	152 (max)
Salt-dome emissions (uncontrolled)	1	2.0		a	a	Ambient	a	a
Flares						b	b	b
98% efficiency	1	1.1	0.017	95	0.73	38[b]	63.6 (max)[b]	152 (max)[a]
90% efficiency	1	5.6	0.083	95	0.73	38[b]	63.6 (max)[b]	152 (max)[a]
Storage tanks (uncontrolled)								
Pyrolysis gasoline	1	0.8	0.11	9.8	9.5			
Storage tanks (controlled)								
Pyrolysis gasoline	1	0.12	0.017	9.8	9.5			
Fugitive emissions (uncontrolled)		24.8	0.18					
Fugitive emissions (controlled)		4.8	0.035					
Secondary emissions (uncontrolled)		0.16	0.06					

[a] Vented from brine storage pond.

[b] Conditions before combustion.

Table B-2. Air-Dispersion Parameters for Model-Plant VIII
(544.2-Gg/yr Ethylene, 50:50 Naphtha/Gas-Oil Feed), Single Compressor Trains

Source	No. of Units	Emission Rate (g/sec)		Height (m)	Dia. (m)	Discharge Temp. (°C)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
		VOC	Benzene					
Naphtha/gas-oil pyrolysis furnace flue gas	6	0.1		40	2.3	171	59	14.1
Ethane/propane pyrolysis furnace flue gas	1	0.1		27.5	4.4	171	24	15.9
Gasoline hydrogenation heater flue gas	1	0.04		39.6	1.2	399	10	9.0
Catalyst regeneration heater flue gas	1	0.01		15.2	0.6	704	4	14.8
Catalyst regeneration off-gas								
Acetylene converter	1			18.3	0.6	510	17	59.1
Gasoline treatment	1			18.3	0.6	510	16	56.7
C_3 converter	1			15.2	0.3	510	4	51.2
Amine stripper vent[a]	1			130	0.1	Ambient	0.065	8.3
Compressor lube-oil vents (uncontrolled)								
Charge gas	1	0.05	0.0008	18.3	0.3	60		
Propylene	1	0.025		18.3	0.3	60		
Ethylene	1	0.025		18.3	0.3	60		
Main vent (uncontrolled)	1	213	13.7	76.2	1.5	38	269 (max)	152 (max)
Salt-dome emissions (uncontrolled)	1	4.7		b	b	Ambient	b	b

Table B-2. (Continued)

Source	No. of Units	Emission Rate (g/sec) VOC	Emission Rate (g/sec) Benzene	Height (m)	Dia. (m)	Discharge Temp. (°C)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Flares						c	c	c
98% efficiency	1	4.3	0.3	130	1.5	38[c]	269[c]	152[c]
90% efficiency	1	21.3	1.4	130	1.5	38[c]	269[c]	152[c]
Storage tanks (uncontrolled)								
Naphtha/gas-oil								
(naphtha emissions only)	2	0.6		12.2	33.4	Ambient		
Raw pyrolysis gas	1	4.8	0.5	14.6	42.7	Ambient		
Treated pyrolysis gas	2	6.7	1.0	12.2	33.0	Ambient		
Storage tanks (controlled)								
Naphtha/gas oil								
(naphtha emissions only)	2	0.3		12.2	33.4	Ambient		
Raw pyrolysis gas	1	0.8	0.14	14.6	42.7	Ambient		
Treated pyrolysis gas	2	0.6	0.12	12.2	33.0	Ambient		
Fugitive emissions (uncontrolled)		25.2	0.79					
Fugitive emissions (controlled)		4.8	0.15					
Secondary emissions (uncontrolled)		1.0	0.38					

[a] Vented at top of main-vent flare stack.

[b] Vented from brine storage pond.

[c] Conditions before combustion.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST ESTIMATE DETAILS

This appendix contains sample calculations showing how the costs presented in this report were estimated.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure D-1 illustrates this relationship. The contingency allowance indicated is included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. D-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternative within the limits of accuracy indicated.

A. STEAM-ASSISTED ELEVATED FLARE CONTROLLING INTERMITTENT EMISSIONS FROM MODEL-PLANT I (ETHANE FEED, 226.8 Gg/yr) WITH SINGLE COMPRESSOR TRAINS

1. Installed Capital Cost

The model plant flares are sized to smokelessly combust the maximum emissions vented during normal startup and shutdown operations. For a plant with naphtha and gas-oil flexibility and producing 589.6-Gg/yr (1.3 billion lb/yr) ethylene the required smokeless capacity was reported to be 243,000 lb/hr.[1] For the model plants the required smokeless capacities are based on this value but are estimated to be proportional to the respective compressor charge-gas rates, as given in Table IV-8 for plants producing 453.5 Gg/yr (1 billion lb/yr) of ethylene from various feedstocks. For Model-Plant I (ethane feed, 226.8 Gg/yr) the required smokeless capacity is determined as follows:

$$243{,}000\ \frac{\text{lb}}{\text{hr}} \times \frac{226.8^{a}}{589.6^{b}} \times \frac{772.0^{c}}{1539.9^{d}} = 46{,}900\ \text{lb/hr}.$$

---

[a] Model-Plant I ethylene capacity, Gg/yr.

[b] Ethylene capacity of plant with required flare smokeless capacity of 243,000 lb/hr.

[c] Charge-gas rate for plant producing 453.5 Gg/yr from ethane.

[d] Charge-gas rate for plant producing 453.5 Gg/yr from 50:50 N/G feed.

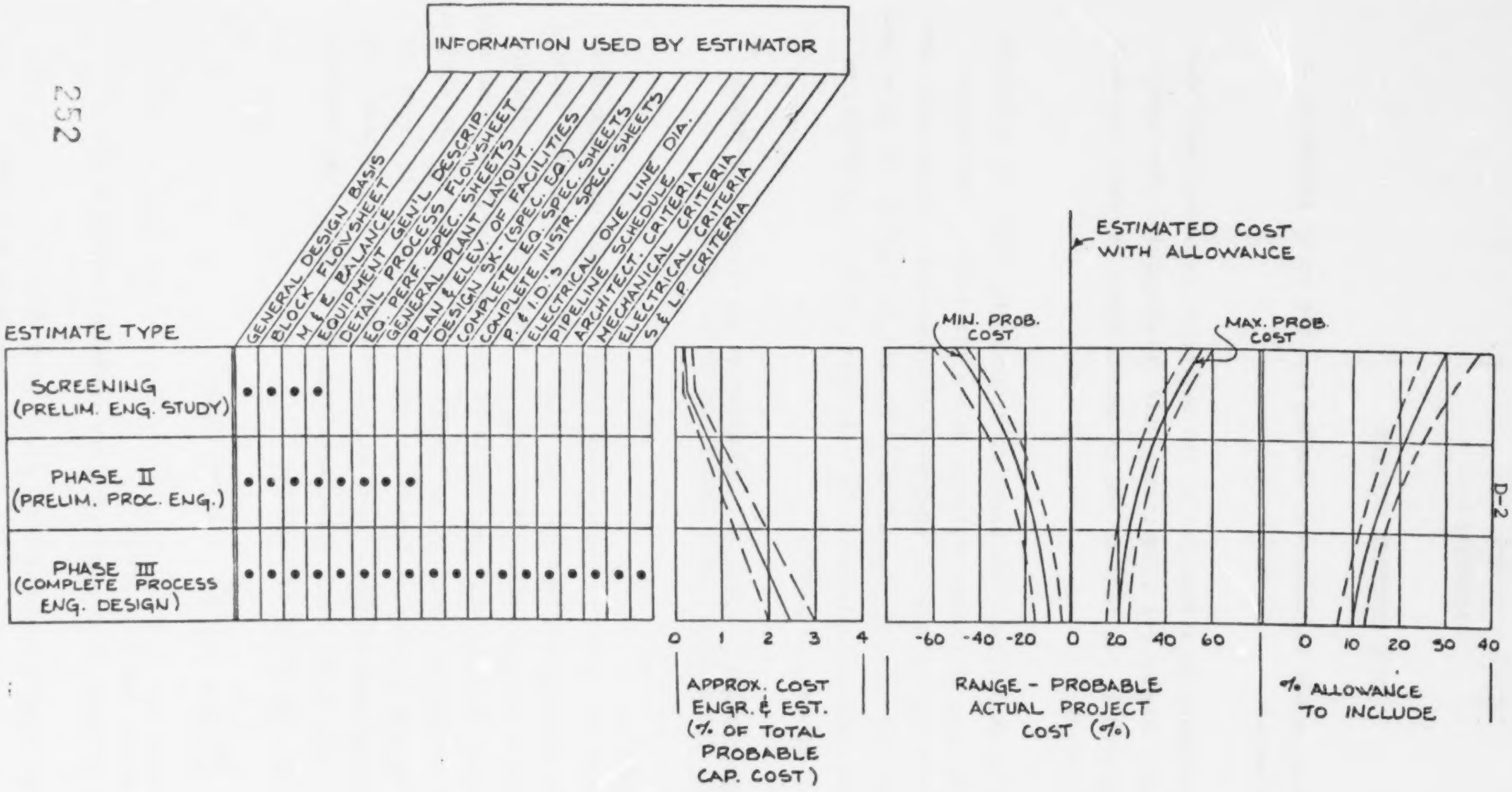

Fig. D-1. Precision of Capital Cost Estimates

From Fig. V-1 of the flare report[2] the installed capital cost of the required elevated flare system is estimated to be $175,000.

2. Gross Annual Operating Cost

From Table VI-1 of this report the total fixed costs, including capital recovery, are 29% of the installed capital cost:

$$\$175,000 \times 0.29 = \$50,800/\text{yr}.$$

From Fig. IV-1 of the flare report[2] the required flare tip diameter is determined as 16 in., and from IV-4 of the flare report the corresponding natural gas used for the pilots is 60 scfh and for purging is 155 scfh. From Table VI-1 the cost of gas is $2.00 per thousand ft^3:

$$(60 + 155) \times 8760 \times \frac{2.00}{1000} = \$3770/\text{yr}.$$

From Sect. IV-A-1 of the flare report it is estimated that 0.3 lb of steam is required per pound of emission; from Table VI-1 the cost of steam is $2.50/thousand lb. From Table IV-3 of this report the average emission from Model-Plant I with single compressor trains is 179 kg/hr (395 lb/hr):

$$0.3 \times 395 \times 8760 \times \frac{2.50}{1000} = \$2600/\text{yr}.$$

The annual cost summary is as follows:

Fixed	$50,800
Natural gas	3,800
Steam	2,600
Total	$57,200

3. Cost Effectiveness

Cost effectiveness is the gross annual operating cost $57,200 divided by the annual VOC or benzene destroyed at 98% or 90% efficiency.* From Tables IV-3 and V-1 of this report the total VOC reduction of intermittent emissions is 1540 Mg/yr at a flare efficiency of 98% and is 1410 Mg/yr at a efficiency of 90%. The total benzene destroyed is 6.6 Mg/yr at 98% flare efficiency and is 6.1 Mg/yr at 90% flare efficiency:

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*Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies used are for tentative comparison purposes.

$\frac{\$57,200}{1540}$ = \$37.1/Mg of VOC destroyed (98% flare efficiency).

$\frac{\$57,200}{1410}$ = \$40.5/Mg of VOC destroyed (90% flare efficiency).

$\frac{\$57,200}{6.6}$ = \$8600/Mg of benzene destroyed (98% efficiency).

$\frac{\$57,200}{6.1}$ = \$9400/Mg of benzene destroyed (90% efficiency).

B. REFERENCES*

1. R. L. Standifer, IT Enviroscience, Trip Report for Arco Chemical Co., Channelview, TX, Aug. 16--17, 1977 (on file at EPA/ESED, Research Triangle Park, NC).

2. V. Kalcevic, IT Enviroscience, Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA/ESED, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX E

INTERMITTENT-EMISSION SAMPLE CALCULATIONS

A. BASE CASE: 50:50 N/G, 453.6-Gg/yr Ethylene

1. Charge-Gas Emissions, Single Compressor Trains

From Table III-1 the 5-year average material loss caused by compressor outages, including hydrogen and methane (total charge gas emissions), for a plant with N/G flexibility (50:50 N/G assumed), single compressor trains, producing 453.6 Gg/yr ethylene is

$$\frac{9878 + 6857 + 5469 + 4653 + 3837}{5} = 6138.7 \text{ Mg/yr} = 700.8 \text{ kg/hr.}^{a}$$

The uncontrolled (nonmethane) VOC emissions are

$$700.8 \times 0.868^{b} = 608.3\text{-kg/hr VOC.}$$

The uncontrolled benzene emissions are

$$700.8 \times 0.0585^{c} = 41.0\text{-kg/hr benzene.}$$

2. Charge-Gas Emissions, Dual Compressor Trains

From Table III-1 for the same plant with dual compressor trains the 5-year average material loss caused by compressor outages (total charge gas emissions) is

$$\frac{1224 + 857 + 735 + 612 + 490}{5} = 783.6 \text{ Mg/yr} = 89.5 \text{ kg/hr.}^{a}$$

The uncontrolled (nonmethane) VOC emissions are

$$89.5 \text{ kg/hr} \times 0.868 = 77.7 \text{ kg/hr.}$$

The uncontrolled benzene emissions are

$$89.5 \text{ kg/hr} \times 0.0585 = 5.2 \text{ kg/hr.}$$

---

[a] Compressor outage material losses (total charge-gas emissions) for the model plants are based on these values as shown by the sample calculations for Model-Plant I.

[b] 86.8% nonmethane VOC in charge gas.

[c] 5.85% benzene in charge gas.

3. Miscellaneous (Other) Intermittent Emissions (Single and Dual Trains)

For the base case (Table III-1 conditions) charge-gas emissions account for 95% of the total intermittent emissions (including hydrogen and methane) for plants with single compressor trains. The remaining 5% intermittent emissions (based on single compressor trains) contain no significant quantities of hydrogen, methane, or benzene. The following miscellaneous intermittent emissions are assumed to be the same for single or dual compressor trains:

$$700.8 \times \frac{0.05}{0.95} = 36.9\text{-kg/hr VOC.}^{a}$$

4. Total Intermittent (Nonmethane) VOC Emissions

For single compressor trains the emissions are

$$608.3 + 36.9 = 645.2 \text{ kg/hr.}$$

For dual compressor trains the emissions are

$$77.7 + 36.9 = 114.6 \text{ kg/hr.}$$

B MODEL-PLANT I (ETHANE FEED, 226.8-Gg/yr ETHYLENE) SINGLE COMPRESSOR TRAINS

1. Charge-Gas Emissions

Estimates of charge-gas emissions for the model plants are based on the estimates developed for the Table III-1 conditions and are assumed to be proportional to the respective quantities of compressor charge gas produced. The charge-gas quantities and compositions used are given in Table IV-8 and are based on the feed requirements and yield structures given in Table II-1:

$$\frac{(551.7 \text{ Gg of ethane} \times 1.4)^{b} - 0.4 \text{ Gg of fuel oil produced}}{453.5 \text{ Gg of ethylene produced}} = 1.702 \text{ Gg of charge gas/Gg of ethylene produced.}$$

For Table III-1 conditions (N/G flexibility) and for the 50:50 N/G model plants (VIII--X), a charge gas:ethylene ratio of 3.395 was estimated based on averages of the naphtha and gas oil value.

---

[a] Miscellaneous intermittent emissions for the model plants are based on this value, as shown by the sample calculations for Model-Plant I.

[b] Based on a recycle ratio of 0.4 for ethane (Table IV-8).

Then the total charge-gas emissions (including hydrogen and methane) for Model-Plant I with single compressor trains are

$$700.8^{a} \times \frac{226.8^{b}}{453.5^{c}} \times \frac{1.70^{d}}{3.395^{e}} = 175.7 \text{ kg/hr.}$$

The uncontrolled nonmethane VOC emissions are

$$175.7 \times 0.914^{f} = 160.6 \text{ kg/hr.}$$

The uncontrolled benzene emissions are

$$175.7 \times 0.0044^{g} = 0.77 \text{ kg/hr.}$$

2. Miscellaneous (Other) Intermittent Emissions

Estimates of miscellaneous intermittent emissions for the model plants are based on the estimates developed for the Table III-1 conditions and are assumed to be proportional to ethylene production. For Model-Plant I the miscellaneous intermittent emissions are

$$36.9 \times \frac{226.8^{b}}{453.6^{c}} = 18.5 \text{ kg/hr.}$$

3. Total Emissions

The total uncontrolled intermittent (nonmethane) VOC emissions for Model-Plant I with single compressor trains are as follows:

$$160.6 + 18.5 = 179.0 \text{ kg/hr.}$$

---

[a] Total charge-gas emissions for Table III-1 conditions, single trains.

[b] Ethylene production, Model-Plant I.

[c] Ethylene production, Table III-1 conditions.

[d] Charge gas:ethylene ratio for ethane feed.

[e] Charge gas:ethylene ratio for 50:50 N/G feed (Table III-1 conditions).

[f] 91.4% nonmethane VOC in charge gas.

[g] 0.44% benzene in charge gas.

4. Controlled Intermittent Emissions

The nonmethane VOC emissions with 98% flare efficiency are

$178.6 \times 0.02^b = 3.6$ kg/hr.

The benzene emissions are

$0.77 \times 0.02^b = 0.015$ kg/hr.

The main-vent flare emissions with 90% flare efficiency are

$178.6 \times 0.10 = 17.9$ kg/hr for VOC

and

$0.77 \times 0.10 = 0.077$ kg/hr for benzene.

APPENDIX F

SALT-DOME STORAGE-EMISSION SAMPLE CALCULATIONS

A. MODEL VIII -- 50:50 N/G FEED, 544.2-Gg/yr ETHYLENE BASIS

Annual throughput, 15 days' ethylene production.

Storage dome conditions, 20°C, 100-atm pressure.

Brine conditions, saturated sodium chloride brine.

1. Throughput of Ethylene

$$(544.2\ \mathrm{Gg/yr})\left(\frac{15}{365}\right) = 22.4\ \mathrm{Gg/yr}.$$

2. Volume of Brine Displaced

Specific volume of ethylene at 20°C, 100 atm:

$$V = \frac{f}{P} \times \frac{V_o^o}{\mathrm{M.W.}}$$

where

f = Compressibility factor
= 0.360,
M.W. = molecular weight,
V_o^o = the volume given in Table 160 of ref. 1
= 22,240,

$$V = \frac{(0.360)(22,240)}{(100)(28)}$$

$$= 2.86\ \mathrm{cc/g} = 2860\ \mathrm{m^3/Gg}.$$

The volume of brine displaced = (22.4)(2860) = 64,064 m^3.

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[1] J. H. Perry, Chemical Engineer's Handbook, 3d ed., pp. 205——208, McGraw-Hill, New York, 1950.

3. Solubility of Ethylene in Brine

The solubility of ethylene in H_2O at 20°C, 100 atm, was calculated as follows:

$$x_a = \frac{P_a}{H},$$

where

x_a = the mole fraction of a in the liquid
$= \frac{100}{10{,}200} = 9.8 \times 10^{-3}$ (ref. 2),

P_a = the partial pressure of component a in the vapor,
H = Henry's law constant (ref. 2).

$$w = x_a \cdot \frac{M_A}{M_S} = (9.8 \times 10^{-3}) \frac{(28)}{(18)} = 15.24 \times 10^{-3} \text{ g of } C_2H_4/\text{g of } H_2O.$$

The solubility of ethylene in saturated NaCl brine was calculated as follows:

$$\text{Solubility of NaCl at 20°C} = 6.1 \frac{\text{g-mole of NaCl}}{1000 \text{ g of } H_2O} \quad \text{(ref. 2)},$$

$$K = \frac{1}{c} \log \frac{S_o}{S} \quad \text{(ref. 3)},$$

where

S_o = solubility of gas in pure H_2O (g/1000 g of H_2O),
S = solubility of gas in solution (g/1000 g of H_2O),
K = 0.134 at 20°C (ref. 4),
$c = \frac{\text{g equiv of salt}}{1000 \text{ g of } H_2O}$.

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[2] *ibid*., pp. 673—675.

[3] N. A. Lange, *Handbook of Chemistry*, 8th ed., 1952, p. 289.

[4] Winkler, "Landolt-Börnstein Physicalisch-Chemische Tabellen."

Then

$$0.134 = \frac{1}{6.1} \log \frac{15.24}{s}$$

and

$$s = 2.32 \times 10^{-3} \text{ g of } C_2H_4/\text{g of } H_2O.$$

4. Ethylene Emission

$$(64064 \text{ m}^3) \left(\frac{1 \text{ Mg}}{\text{m}^3}\right) \left(2.32 \times 10^{-3} \frac{\text{g of } C_2H_4}{\text{g of } H_2O}\right) = 148.6 \text{ Mg/yr.}$$

The average VOC emission rate = 17.0 kg/hr.

3. Maximum Emission Rate

Assuming that an average of 15 days' production is moved in and out of storage, the maximum emission rate is

$$17.0 \text{ kg/hr} \times \frac{365}{15} = 410 \text{ kg/hr.}$$

APPENDIX G

LIST OF EPA INFORMATION SOURCES*

1. R. B. Ruston, EPA questionnaire for Allied Chemical Corporation, Geismar Complex, Geismar, Louisiana.
2. G. Delodder, EPA questionnaire for Union Carbide Corporation, Texas City Plant, Texas City, Texas.
3. W. R. Chalker, EPA questionnaire for E. I. du Pont de Nemours and Company, Sabine River Works, Orange, Texas.
4. H. McNair, EPA questionnaire for Dow Chemical Company, Plant A and Plant B, Freeport, Texas.
5. D. G. Pringle, EPA questionnaire for Texas Eastman Company, Longview, Texas.
6. C. B. Brantley, EPA questionnaire for Gulf Oil Company, Port Arthur Refinery, Port Arthur, Texas.
7. H. J.LaBorde, EPA questionnaire for Northern Petrochemical Company, Joliet Plant, Morris, Illinois.
8. R. L. Maycock, EPA questionnaire for Shell Chemical Company, Houston Chemical Plant, Deer Park, Texas.
9. H. M. Walker, EPA questionnaire for Monsanto Company, Chocoloate Bayou Plant, Alvin, Texas.
10. D. W. Smith, letter to EPA from E. I. du Pont de Nemours & Company, February 3, 1978.
11. J. P. Walsh, letter to EPA from Exxon Chemical Co., February 10, 1978.
12. R. J. Brenner, letter to EPA from Mobil Chemical Co., January 26, 1978.
13. L. A. McReynolds, letter to EPA from Phillips Petroleum Co., January 27, 1978.
14. A. G. Smith, letter to EPA from Shell Oil Company, February 22, 1978.

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*Sources 1--9 were part of a data-gathering program in the preparation of *Survey Report on Atmospheric Emissions from the Petrochemical Industry*, Vol. II, by J. W. Pervier *et al.*, EPA-450/3-73-005-b (April 1974).

APPENDIX H

EXISTING PLANT CONSIDERATIONS

A. EXISTING PLANT CHARACTERIZATION

Table H-1 lists emission control devices reported to be in use by industry.[1--8] To gather information for the preparation of this report two site visits were made to manufacturers of ethylene. Trip reports have been cleared with the companies concerned and are on file at EPA, ESED, in Durham, NC; EPA also has received letters in response to requests for information on air emissions from ethylene plants and in response to requests for comments on the draft version of this report. Some of the pertinent information concerning process emissions from existing ethylene plants is presented in this appendix.

1. Arco Chemical Co., Channelview, TX (Lyondell Plant)[1]

Two nearly identical olefin units, designed and engineered by the Lumus Company, are located at the Lyondell plant. At the time of the site visit (August 1977) Olefin unit No. 1 had been in operation for less than one year and construction of Olefin unit No. 2 was nearing completion. Each unit has an annual design capacity of 1.3 billion lb of ethylene. Feedstocks for both units are naphtha and/or gas oil.

The more significant VOC emission control devices include two flares and their associated equipment and a brine degassing system associated with product storage in underground salt domes. Possibly of greater significance in the control of VOC emissions are some of the internal features of the process. Most notable among these are (1) the recycle of most wastewater to the process, (2) the generation and effective recycle of steam from process wastewater, (3) the use of high-capacity centrifugal compressors designed for low emission levels, (4) the transfer of all products by pipeline,minimizing transfer losses, and (5) the routing of most relief valves and process vents to the flare system. Table H-2 summarizes Arco's estimates of controlled VOC emissions from the No. 1 olefin unit. Not included are estimates of uncontrolled intermittent emissions, VOC emissions discharged from the flare system, or fugitive or secondary emissions.

The steam-assisted elevated flare for the No. 1 olefin unit is designed to smokelessly burn up to 243,000 lb/hr of hydrocarbons, the maximum anticipated flaring rate during normal startup and shutdown. The maximum design capacity of the

Table H-1. Control Devices Currently Used by the United States Ethylene Industry

Company	Location	Control Devices and Techniques for Various Emission Sources			
		Intermittent	Lube-Oil Vents	Atmospheric Storage Tanks	Salt-Dome Storage
Arco[a]	Channelview, TX	Elevated flare	High-efficiency seals[b]	Floating-roof tanks	Flare
Gulf[c]	Cedar Bayou, TX				
1591 (E/P) unit		Elevated flare	None	Floating-roof tanks	Storage contracted
1592 (N/G) unit		Elevated flare	High-efficiency seals[b]	Floating-roof tanks	
Mobil[d]	Beaumont, TX	Elevated flare	Not reported	Not reported	Not reported
Texaco[e]	Port Neches, TX	Elevated flare	None	Not reported	Not reported
Texas-Eastman[f]	Longview, TX				
Absorption plant		Horizontal flare	Not reported	Not reported	Not reported
Cryogenic plant		Horizontal flare	Not reported	Not reported	Not reported
Du Pont[g]	Orange, TX	Elevated flare	Not reported	Floating-roof tanks	Not reported
Phillips[h]	Sweeny, TX	Elevated flare	Not reported	Not reported	Not reported
Shell[i]	Deer Park, TX	Elevated flare	Not reported	Not reported	Not reported
Exxon[j]	Baton Rouge, LA	Elevated flare	70% controlled by flaring	Not reported	C_2H_4 storage contracted, C_3H_6 controlled with 25—30 ft brine "buffer" zone

[a] See ref 1.

[b] Total emissions only 0.6 lb/hr.

[c] See ref 2.

[d] See ref 8.

[e] See ref 3.

[f] See ref 4.

[g] See ref 5.

[h] See ref 6.

[i] See ref 7.

[j] See ref 2.

Table H-2. Estimated Emissions from Arco-Lyondell Plant Olefin Unit No. 1 (Naphtha/Gas Oil Feed)[a]

Source	Average VOC Emissions (lb/hr)
Naphtha storage	15
Pyrolysis gasoline storage	27
Other storage tanks	0.2
Lube-oil vents	0.6

[a] See ref 1.

flare (not smokeless) is 2.3 million lb/hr of hydrocarbons. All process relief valves except those relieving the demethanizer column are vented to the flare system. Emissions from the demethanizer relief valves would be primarily hydrogen and methane.

2. Gulf Oil Chemicals Co., Cedar Bayou, TX[2]

Two olefin units are located at this plant. The older of the two units (unit 1591), which has been in operation since 1963, has a rated ethylene capacity of 400 million lb/yr. Feedstocks for this unit are ethane and propane. The newer unit (unit 1592), designed and engineered by the Lumus Company, was started in 1976 and has a rated ethylene production capacity of 1.2 billion lb/yr. Feedstocks are naphtha and/or gas oil. The primary emission control devices for both units are steam-assisted elevated flares. Estimated emissions from both units are given in Tables H-3 and H-4. Not included are estimates of uncontrolled intermittent emissions, VOC emissions discharged from the flare system, or fugitive or secondary emissions.

3. Exxon Chemical Co., Baton Rough, LA[9]

Exxon's Baton Rouge chemical plant (BRCP) has an ethylene production capacity of 695.3 Gg/yr. The BRCP is an older plant that has gone through many modifications, with new equipment incorporated with older, existing equipment. At the BRCP, sidestreams are sent to other units and are converted to products such as butadiene, isobutylene, *n*-butylene, and isoprene. A detailed list of products is provided in Table H-5. A simplified description of the BRCP is that it consists of two single compressor train units. However, the ethylene complex is further broken down into three gas oil cracking sections, two ethane/propane gas cracking sections, and two purification sections.

Table H-6 presents a comparison between Exxon's estimates of uncontrolled intermittent and lubricating-oil vent emissions and emission ratios for the BRCP with those for model-plant VII. The experience at Exxon's BRCP has been that upset emissions resulting from compressor outages do not decrease after the first 5 years of operation.

4. Texaco, Port Neches, TX[3]

Texaco operates two older ethane/propane feedstock units at Port Neches. Following are general comments concerning emission sources and controls for these older units:

Table H-3. Estimated Emissions from Gulf Oil Chemicals Co., Cedar Bayou, TX, 1591 Olefin Unit (Ethlene/Propane Feed)[a]

Source	Average VOC Emissions (lb/hr)
Storage tanks	21
Propylene compressor	18
Cracked-gas compressor	24
Flue gas	3

[a] See ref 2.

Table H-4. Estimated Emissions from Gulf Oil Chemicals Co., Cedar Bayou, TX, 1592 Olefin Unit (Naphtha/Gas Oil Feed)

Source	Average VOC Emissions (lb/hr)
Flue gas	12
Naphtha storage	0.9
Pyrolysis gasoline storage	31
Other storage tanks	0.2
Lube-oil vents	0.6

[a] See ref 2.

Table H-5. Exxon Baton Rouge Chemical Plant Olefin Unit Products[a]

Major Products	Indirect Products
Tar	Isopropanol (from propylene)
Aromatic high boilers	Petroleum resins
Low-pressure distillate	Chlorobutyl rubber
Heartcut distillate	Other rubbers
Heavy naphtha	
Hydrogen	
Tail gas	
Ethylene	
Propylene	
Isobutylene	
Butadiene	
Isoprene	
Other by-product streams	

[a] See ref 3.

Table H-6. Comparison of Benzene and Total VOC Uncontrolled Emissions from Selected Sources from the Exxon BRCP with Model-Plant-VII Emissions[a]

Source	Emission Ratio (g/Mg)[b]		Emission Rate (kg/hr)[c]	
	Benzene	Total VOC	Benzene	Total VOC
Lube oil vents				
Exxon BRCP - precontrolled	2.33	280	0.145	17.4
Exxon BRCP - after large volume vents controlled	0.655	27.6	0.041	1.71
Model Plant VII, single trains	0.206	5.79	0.0128	0.36
Intermittent emissions				
Exxon BRCP		14,100		876.1[d]
Model Plant VII, single trains	792	12,300	49.2	765.0

[a] See ref 3.

[b] g of benzene or VOC per Mg of ethylene produced.

[c] Exxon BRCP emissions prorated to model-plant-VII ethylene capacity.

[d] 97% of Exxon BRCP intermittent emissions are flared.

a. Compressor lubricating-oil vents—no buffer gas in seals and the seal oil is routed to an oil/water collection system, which, in turn, is vented to the atmosphere through a carbon filter.

b. Furnace stack and decoking gases—vented to the atmosphere.

c. Compressor outage emissions—vented to the flare.

d. Relief valves—the quench tower relief valve is vented to the flare; the recovery section relief valves are vented to the atmosphere; however, during normal operation the pressure control on the towers is maintained by venturi to the flare system.

e. Analyzers are vented to the atmosphere.

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

C. REFERENCES*

1. R. L. Standifer, IT Enviroscience, Trip Report for Arco Chemical Co., Channelview, TX, Aug. 16, 17, 1977 (on file at EPA/ESED, Research Triangle Park, NC).

2. R. L. Standifer, IT Enviroscience, Trip Report for Gulf Oil Chemicals Co., Cedar Bayou Oletius Plant, Cedar Bayou, TX, Sept. 13, 14, 1977 (on file at EPA/ESED, Research Triangle Park, NC).

3. J. F. Cooper, Texaco, Inc., letter dated Feb. 2, 1979, to EPA with information on ethylene processes at Port Arthur and Port Naches, TX, in response to EPA request for comments on ethylene draft report.

4. G. Prendergast, Texas Eastman Co., letter dated Feb. 21, 1978, to EPA with information on ethylene processes at Longview, TX, in response to EPA request for information.

5. D. W. Smith, Dupont, letter dated Feb. 3, 1978, to EPA with information on ethylene processes at Orange, TX, in response to EPA request for information.

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8. P. B. Mullin, Mobil Chemical Co., letter dated Jan. 26, 1978, to EPA with information on ethylene processes at Beaumont, TX, in response to EPA request for information.

9. J. P. Walsh, Exxon Chemical Co., letter dated Feb. 26, 1979, to EPA with information on ethylene processes at Baton Rouge, LA, in response to EPA request for comments on Ethylene draft report.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 4

ETHYLENE OXIDE

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CONTENTS OF REPORT 4

		Page
I.	ABBREVIATIONS AND CONVERSION FACTORS	I-1
II.	INDUSTRY DESCRIPTION	II-1
	A. Reason for Selection	II-1
	B. EO Usage and Growth	II-1
	C. Domestic Producers	II-1
	D. References	II-7
III.	PROCESS DESCRIPTIONS	III-1
	A. Introduction	III-1
	B. Oxidation of Ethylene	III-1
	C. References	III-7
IV.	EMISSIONS	IV-1
	A. Air-Oxidation Process	IV-1
	B. Oxygen-Oxidation Process	IV-5
	C. References	IV-13
V.	APPLICABLE CONTROL SYSTEMS	V-1
	A. Air-Oxidation Process	V-1
	B. Oxygen-Oxidation Process	V-5
	C. References	V-10
VI.	IMPACT ANALYSIS	VI-1
	A. Environmental and Energy Impacts	VI-1
	B. Control Cost Impact	VI-5
	C. Reference	VI-16
VII.	SUMMARY	VII-1

APPENDICES FOR REPORT 4

		Page
A.	PHYSICAL PROPERTIES OF ETHYLENE AND ETHYLENE OXIDE	A-1
B.	AIR-DISPERSION PARAMETERS	B-1
C.	FUGITIVE-EMISSION FACTORS	C-1
D.	COST ESTIMATE DETAILS	D-1
E.	EXISTING PLANT CONSIDERATIONS	E-1

TABLES OF REPORT 4

Number		Page
II-1	Ethylene Oxide Usage and Growth	II-2
II-2	Ethylene Oxide Capacity	II-3
IV-1	Uncontrolled Emissions for Air-Oxidation Process	IV-2
IV-2	Main Process Vent Compositions, Air-Oxidation Process	IV-4
IV-3	Stripper Purge Vent Composition, Air-Oxidation Process	IV-4
IV-4	Model Plant Storage, Air-Oxidation Process	IV-6
IV-5	Uncontrolled Emissions for Oxygen-Oxidation Process	IV-8
IV-6	CO_2 Purge Vent Composition, Oxygen-Oxidation Process	IV-8
IV-8	Stripper Purge Vent Composition, Oxygen-Oxidation Process	IV-11
IV-7	Argon Purge Vent Composition, Oxygen-Oxidation Process	IV-9
IV-9	Model Plant Storage, Oxygen-Oxidation Process	IV-11
V-1	Controlled Emissions for Air-Oxidation Process	V-2
V-2	Controlled Emissions for Oxygen-Oxidation Process	V-6
VI-1	Emission Reduction by Control Devices for Air-Oxidation Process	VI-2
VI-2	Emission Reduction by Control Devices for Oxygen-Oxidation Process	VI-4
VI-3	Cost Factors Used in Computing Annual Costs	VI-6
VI-4	Emission Control Cost Estimates for Model Plants Using Oxygen-Oxidation or Air-Oxidation Process	VI-7
VII-1	Emission Summary, Air-Oxidation Process	VII-2
VII-2	Emission Summary, Oxygen-Oxidation Process	VII-2
A-1	Properties of Ethylene	A-1
A-2	Properties of Ethylene Oxide	A-2
B-1	Air-Dispersion Parameters for Air-Oxidation Model Plant	B-1
B-2	Air-Dispersion Parameters for Oxygen-Oxidation Model Plant	B-2

TABLES (continued)

Number		Page
D-1	Emission Flow Data	D-3
D-2	Catalytic Oxidizer Control Cost Data for Air-Oxidation Process	D-5
D-3	Thermal Oxidizer Control Cost Data for Air-Oxidation Process	D-6
D-4	Stripper Purge Vent Control Cost Data for Air-Oxidation Process	D-7
D-5	Stripper Purge Vent Control Cost for Oxygen-Oxidation Process	D-8
E-1	Emission Control Devices Used by Some Domestic Ethylene Oxide Procedures	E-2
E-2	Emission Data for Process Vents	E-5

FIGURES OF REPORT 4

Number		Page
II-1	Location of Plants Manufacturing Ethylene Oxide	II-4
III-1	Flow Diagram for Air-Oxidation Process	III-3
III-2	Flow Diagram for Oxygen-Oxidation Process	III-5
VI-1	Capital Cost for Emission Control, Air-Oxidation Process	VI-8
VI-2	Annual Cost for Emission Control, Air-Oxidaton Process	VI-9
VI-3	Cost Effectiveness for Emission Control, Air-Oxidation Process	VI-10
VI-4	Capital Cost for Emission Controls for Oxygen-Oxidation Process	VI-13
VI-5	Annual Cost for Emission Controls Oxygen-Oxidation Process	VI-14
VI-6	Cost Effectiveness for Emission Control, Oxygen-Oxidation Process	VI-15
D-1	Precision of Capital Cost Estimates	D-2

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Ethylene oxide (EO) production was selected as a product for study because of the indication by preliminary data of relatively high total emissions of volatile organic compounds (VOC), of the suspicion of harmful health effects caused by EO,[1] and of the expected industry growth.[2]

Although EO generally is handled as a liquid, it is a gas at ambient conditions (see Appendix A for pertinent physical properties of EO). The largest process emission is unreacted ethylene, the organic raw material for EO production.

B. EO USAGE AND GROWTH

Table II-1 shows EO end products and their expected growth rates. The predominant end use is the production of ethylene glycol, from which antifreeze and polyethylene terephthalate fibers and films are made.

The domestic annual production capacity for EO on July 1, 1979, was estimated to be 2783 Gg and the 1978 production was 82% of this capacity. Historically, the industry has operated at approximately 87% of nameplate capacity. Industry capacity is projected to be 3366 Gg by the end of 1981, and consumption by 1983 is expected to be about 2900 Gg.[2]

A substitute feedstock for producing EO is reported to be under development by Union Carbide.[3] No information is available on this development; therefore it will not be covered in this report.

C. DOMESTIC PRODUCERS

As of July 1, 1978, eleven producers of EO in the United States were operating 16 plants at 14 locations. Table II-2 lists the producers and the processes being used; Fig. II-1 shows the plant locations. Approximately 63% of the present domestic capacity is produced by air oxidation of ethylene and 37% by oxygen oxidation of ethylene.

Table II-1. Ethylene Oxide Usage and Growth[a]

End Use	Production for 1978 (%)	Average Growth for 1978—1983 (%/yr)
Ethylene glycol	58.7	5.0—6.0
Diethylene glycol	4.6	4.0—5.0
Triethylene glycol	2.5	4.0—5.0
Polyethylene glycol	2.7	4.5—5.5
Glycol ethers	7.8	4.5—5.5
Ethanolamines	6.3	4.5—5.5
Nonionic surface active agents	12.0	4.0—5.0
Other	5.4	
Total	100	4.5—5.5

[a] Ref 2.

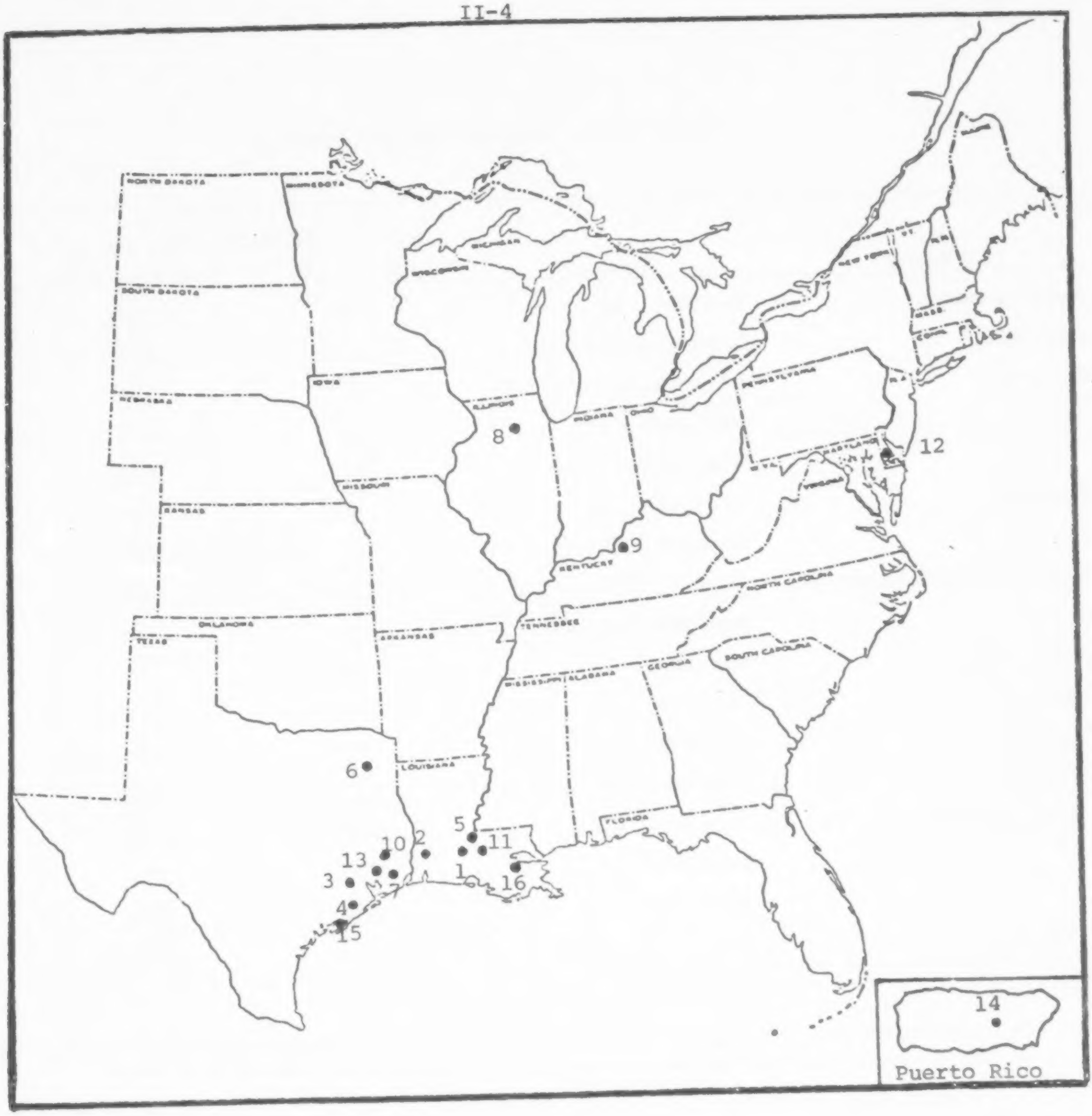
Table II-2. Ethylene Oxide Capacity

Company	Location	Capacity (Gg)[a] July 1, 1979	Capacity (Gg)[a] Year-End 1981	Process[b]
BASF Wyandotte	Geismar, LA	155	218	Oxygen
Calcasieu	Lake Charles, LA		102[c]	Oxygen
Celanese	Clear Lake City, TX	193	193	Oxygen
Dow	Freeport, TX	118	118	Air
	Plaquemine, LA	204	204	Air
Eastman	Longview, TX	88	88	Oxygen
ICI	Bayport, TX		227	Oxygen
Northern Petrochemical	Joliet, IL	104	104	Oxygen
Olin	Brandenburg, KY	50	50	Oxygen
PPG	Beaumont, TX	68	68	Oxygen
Shell	Geismar, LA	318	318	Oxygen
SunOlin	Claymont, DE	45	45	Oxygen
Texaco	Port Neches, TX	215	315	Air
Union Carbide	Penuelas, PR	268	290	Air
	Seadrift, TX	417	477	Air
	Taft, LA	540	578	Air
Total		2783	3366	

[a] See ref 2.

[b] Air is listed for plant believed to be using air as the oxidant feed and oxygen is listed for plants believed to be using purified oxygen as the oxidant feed.

[c] Plant was shut down in early 1978 after an explosion and fire; was to have resumed operation in late 1979.



1. BASF Wyandotte Corp., Geismar, LA
2. Calcasieu Chemical Corp., Lake Charles, LA
3. Celanese Chemical Co., Clear Lake City, TX
4. Dow Chemical Co., Freeport, TX
5. Dow Chemical Co., Plaquemine, LA
6. Eastman Kodak Co., Longview, TX
7. ICI, Bayport, TX
8. Northern Petrochemical Co., Joliet, IL
9. Olin Corp., Brandenburg, KY
10. PPG Industries, Inc. Beaumont, TX
11. Shell Chemical Co., Geismar, LA
12. Sunolin Chemical Co., Claymont, DE
13. Texaco, Port Neches, TX
14. Union Carbide Corp., Ponce, PR
15. Union Carbide Corp., Seadrift, TX
16. Union Carbide Corp., Taft, LA

Fig. II-1. Locations of Plants Manufacturing Ethylene Oxide

The choice of process (air vs oxygen) is based on the cost of ethylene, on the cost of energy, and on other considerations. The air-oxidation process is more adaptable to large units, and results in a lower total investment. The oxygen-oxidation process results in a high ethylene yield and is adaptable to any unit size.[4]

Producing Companies

1. BASF Wyandotte Corp.

   This facility has two production trains, one built in 1957 and one in 1967,[5] with a combined capacity of 155 Gg/yr.[2] The plant built in 1957 was the first commercial use of the oxygen-oxidation process.[6]

2. Calcasieu Chemical Corp.

   The Lake Charles, LA, facility expanded its annual capacity from 74,800 Mg to 104,000 Mg in 1976. A fire in early 1978 shut down this facility; it was to have resumed operation in late 1979.

3. Celanese Chemical Co.

   Much of the EO from the 193-Gg/yr plant is used to produce ethylene glycol for captive use.[2] The plant, built in 1967, uses a process licensed from Shell.[7]

4. Dow Chemical Co.

   Dow's combined production from two separate plants is 322 Gg/yr, most of which is used captively to produce glycols, glycol ethers, and ethanolamines.[2]

5. Texas Eastman Co.

   The major portion of the EO from the 88-Gg/yr capacity is used to produce mono-, di-, and triethylene glycols and glycol ethers.[2]

6. Northern Petrochemical Co.

   Some of the EO produced is marketed; the remainder is converted to glycols.[8]

7. Olin Corp.

   The 50-Gg/yr plant produces EO that is used captively to produce glycols, glycol ethers, ethanolamine, and ethoxylated phenol.[2]

8. PPG Industries

PPG expanded the capacity at their Beaumont, TX, plant from 30 to 68 Gg/yr in 1977. The EO is used captively to produce glycols, with a very small amount going to glycol ethers.[2]

9. Shell Chemical Co.

Shell's plant in Geismar, LA, can produce 318 Gg of EO per year.[2]

10. SunOlin Cemical Co.

The plant can produce 45 Gg of EO per year; all the EO is marketed.[2]

11. Texaco

The EO produced by this 215-Gg/yr plant is used for producing glycols (mono-, di-, tri-, and polyethylene), glycol ethers, ethanolamines, ethoxylated phenols, and mixed linear alcohols.[2]

12. Union Carbide Corp.

Union Carbide, the largest producer of EO, has three plants, with a total capacity of 1,225 Gg/yr.[2] Their Taft, LA, facility is adjacent to an ethylene oxide--glycol handling and shipping complex, reported to be the world's largest.[9]

D. REFERENCES*

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2. S. A. Cogswell, "Ethylene Oxide," pp. 654.5031A—654.5033F, in *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, CA (January 1980).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

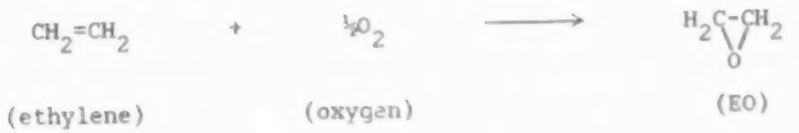
A. INTRODUCTION

In the United States two major processes are used in the manufacture of ethylene oxide (EO); 37% is manufactured at eight locations by oxygen oxidation of ethylene, and 63% at six locations by air oxidation of ethylene. Both processes are projected to continue to grow.

Another process -- the chlorohydrin process -- was the main method of manufacture of EO until 1957 but is no longer used. In 1972 Dow Chemical converted the remainder of its chlorohydrin capacity to the production of propylene oxide.[1]

B. OXIDATION OF ETHYLENE

In commercial processes the direct oxidation of ethylene to ethylene oxide is carried out in the vapor phase, with either air or oxygen used as the oxidant and with a silver catalyst. Oxidation takes place according to the reaction



A second reaction is

$$\underset{\text{(ethylene)}}{CH_2{=}CH_2} + \underset{\text{(oxygen)}}{3O_2} \longrightarrow \underset{\text{(carbon dioxide)}}{2CO_2} + \underset{\text{(water)}}{2H_2O}$$

Under optimum conditions the reactor variables are controlled to give less than 30% per-pass ethylene conversion, which with a fresh catalyst gives a selectivity in the range of 70%, with most of the remainder being converted to CO_2 and water. A higher per-pass ethylene conversion or catalyst aging results in a selectivity shift from EO to CO_2. Catalyst aging is sensitive to the conditions that it is subjected to and catalyst life can run from a very short time up to maybe 5 years. One producer changes the catalyst when selectivity drops to approximately 60%.[2]

1. Air Oxidation of Ethylene

Figure III-1 is a typical flow diagram for a continuous air-oxidation process. Ethylene and air (Streams 1 and 2) are added to a recycle stream (Stream 3), which feeds one or more primary reactors operated in parallel. The fresh air: ethylene feed ratio, usually about 10:1, is varied with the recycle gas to ensure an optimum oxygen:ethylene ratio. Oxidation takes place over a silver catalyst packed in tubes. The reactor is surrounded by a heat transfer fluid to control the temperature; the reaction temperature and pressure are maintained at 220 to 280°C and 1 to 3 MPa. The unreacted ethylene is separated from the reaction products and recycled through the reactor until consumed.[3]

The effluent from the primary reactor (Stream 4) is cooled by the recycle stream from the main absorber (Stream 3) to about 38°C in a shell-and-tube heat exchanger.[4] It is then compressed before entering the main absorber. It passes up the main absorber countercurrent to cold water,[4] in which the EO, along with some of the carbon dioxide from the stream, dissolves. The water solution is removed from the base of the main absorber (Stream 5).[5]

Unabsorbed gas passing overhead from the main absorber is split into two unequal portions.[4] The larger portion (Stream 3) recycles through the reactor effluent cooler and joins the fresh reactor feed. The smaller portion (Stream 6) is passed through a heat exchanger to raise its temperature and then enters the purge reactor (secondary ethylene conversion reactor). The effluent from the purge reactor (Stream 7) is cooled by the incoming feed to the purge reactor and enters the purge absorber, where ethylene oxide is removed from the stream with water, as in the main absorber. The overhead gas (Vent A) is vented from the purge absorber.[4,5] There can be more than one stage of purge reaction, depending on the economics of the value of ethylene recovered versus cost.

The dilute water solutions containing ethylene oxide, carbon dioxide, and other VOC from both absorbers are combined (Stream 8).[4] The mixture is fed to the top of the desorber, where the crude EO (Stream 9) is distilled off the top and compressed for further refining.[4] A stripper removes carbon dioxide and inert gases overhead (Vent B), and the EO, stripped of carbon dioxide (Stream 10), is fed to the midsection of the refiner, where it is distilled overhead to

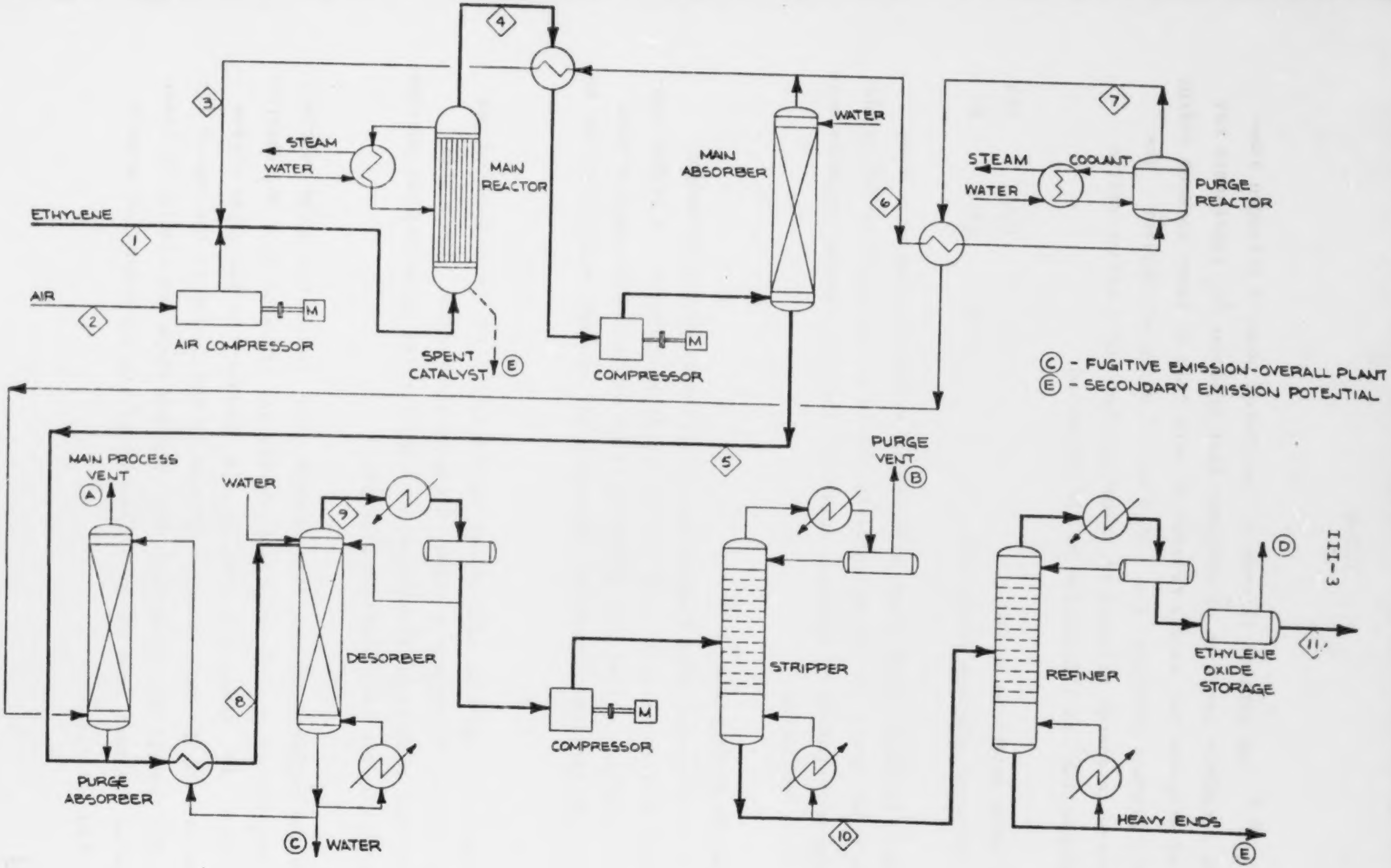


Fig. III-1. Flow Diagram for Uncontrolled Model Plant for Production of Ethylene Oxide by Continuous Air-Oxidation Process

99.5 mole % EO.[4,6] The product (Stream 11) is stored under a nitrogen atmosphere.[4] The secondary reaction of ethylene that produces CO_2 represents not only a loss of ethylene but also a release of more than 13 times as much energy as the primary product reaction, i.e., 50.4 vs 3.7 MJ/kg of ethylene. The large difference in energy released by oxidation when the reaction shifts toward CO_2 production[4] is illustrated by the following:

Selectivity ratio (ethylene to EO)	70%	60%	50%
Total heat, MJ/kg of ethylene converted	17.8	22.5	27

A 227,000-Mg/yr ethylene oxide plant with 70% EO selectivity would release 400 GJ of heat per hour. If the selectivity should be decreased to 50% as the result of improper control or catalyst activity, the heat release would be more than doubled, or 900 GJ/hr.[4]

2. Oxygen Oxidation of Ethylene

Figure III-2 is a typical flow diagram for a continuous oxygen-oxidation process, which differs slightly from the air-oxidation process. A higher concentration of ethylene allows more ethylene to be converted per pass without exceeding the 30% ethylene conversion favorable for optimum selectivity for EO formation.

The oxygen-oxidation process also allows recirculation of the unabsorbed gas through the reactor to achieve a higher ultimate conversion. The higher ultimate ethylene conversion eliminates the need for the purge-reactor absorber system required by the air-oxidation process.

As shown by the oxygen-oxidation flow diagram, Fig. III-2, the purge reactor and purge absorber of the air-oxidation process are replaced by a CO_2 absorber and reactivator. EO, along with some CO_2, is dissolved in the water stream leaving the base of the main absorber (Stream 6) and is fed to the top of the desorber. The desorption, stripping, and refining steps are similar to those of the aqueous effluent from the main absorber of the air-oxidation process (Stream 8, Fig. III-1).[4,5]

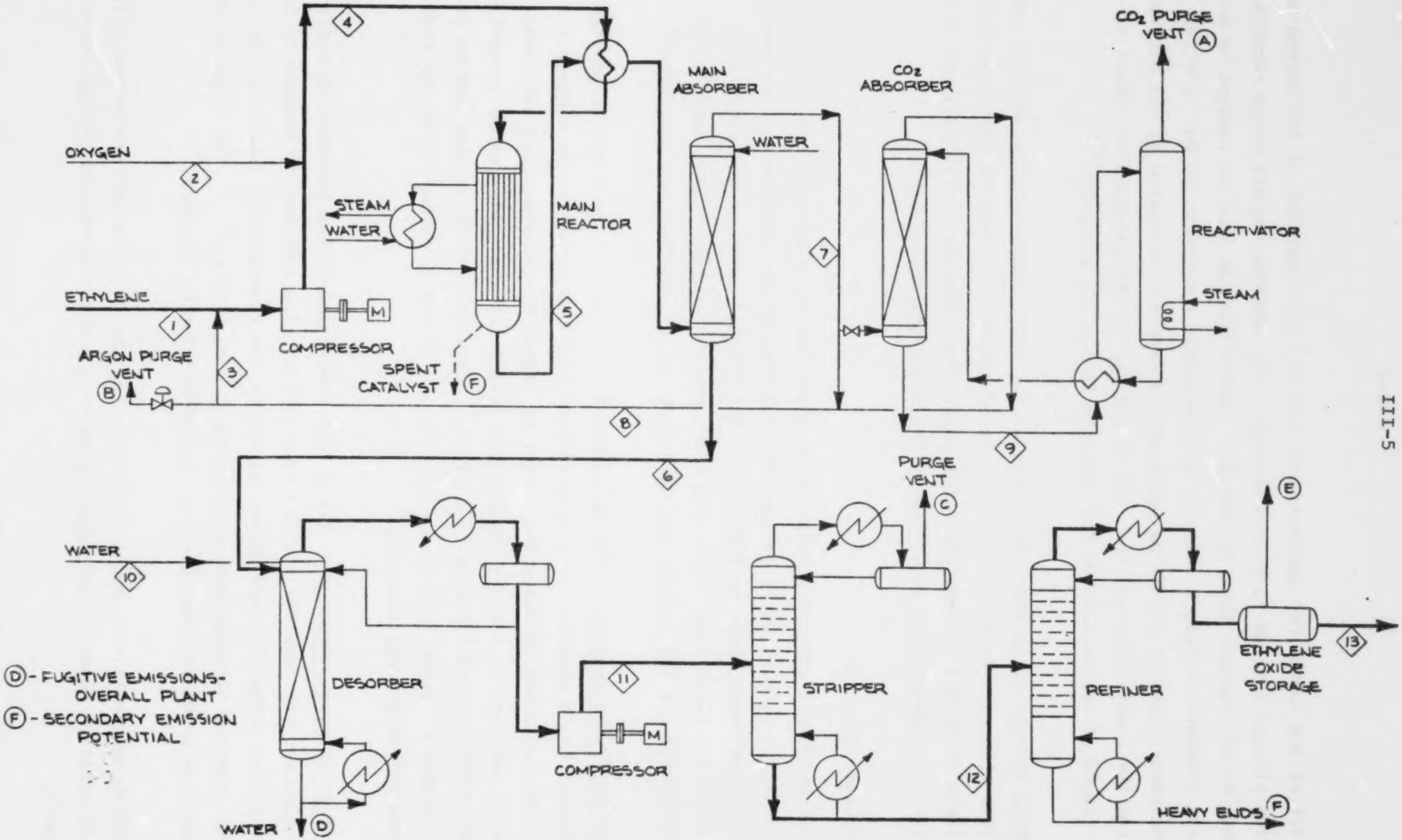


Fig. III-2. Flow Diagram for Uncontrolled Model Plant for Production of Ethylene Oxide by Continuous Oxygen-Oxidation Process

Part of the unabsorbed gas overhead from the main absorber of the oxygen-oxidation process (Stream 7) passes through a CO_2 absorber before being recycled back to the reactor feed (Stream 8). Carbon dioxide must be removed to maintain favorable catalyst activity and favorable conversion to EO. The CO_2 absorbent, usually potassium carbonate (Stream 9), is heated by the bottoms from the reactivator and then fed to the top of the reactivator, where it is stripped of carbon dioxide and recycled to the CO_2 absorber.[4,5]

Small amounts of gaseous impurities in the feed, such as argon, must be removed since they will accumulate in the closed system.[5,7] Some of the recycle gas stream is purged through the argon purge vent (Vent B). This emission flow rate is automatically regulated by the argon concentration.[6]

3. Process Variation

Some producers captively react EO to glycol or to other products in adjoining facilities without purification and isolation of EO. In these cases some of the purge vents shown on Figs. III-1 and 2 would exist in the integrated facility. Also, Figs. III-1 and 2 are general process schemes and do not illustrate all the process and operation variations that are practiced.[2]

a. Air-Oxidation Process -- The model plant, Fig. III-1, has a two-stage reaction system, which consists of a main reactor followed in series by a purge reactor. Large plants may increase the number of stages by incorporating additional purge reactors in series. Additional stages increase the freedom to optimize the reaction conditions of each stage.[8] This results in an improved EO yield by higher ethylene reaction selectivity to EO and in reduction of the ethylene lost in the process vent gas.[8]

b. Oxygen-Oxidation Process -- Yield improvements have been achieved by introducing methane into the reactor feed stream. The addition of methane to the ethylene/ oxygen mixture serves to narrow the flammability limits of the inlet gas, thereby allowing greater feed ratio flexibility.[3,6,7] The argon purge vent gas produced (Vent B) then is suitable for boiler fuel.[9]

Operating conditions, such as pressure, of the CO_2 absorber system can affect the relative quantity and composition of the material vented through Vents A and B.[2]

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Sections 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation. It should be noted that, although ethane is included in VOC emission totals in this report, it does not, based on current research data, participate in ozone-forming reactions to an appreciable extent.

A. AIR-OXIDATION PROCESS

1. Model Plant

The model plant* for this study has an EO capacity of 227 Mg/yr, typical for the industry; this capacity is based on 8760 hr of operation annually.** The model air-oxidation process shown in Fig. III-1 reflects today's manufacturing and engineering technology. Single process trains with multiple, parallel, main reactors and with at least one purge reaction stage are typical. Characteristics of the model plant important to air dispersion are shown in Table B-1 in Appendix B.

2. Sources and Emissions

Sources and emission rates for the air-oxidation process are summarized in Table IV-1. They are meant to represent the typical emissions for the model process; actual emissions of a producer could vary widely for an individual source but the overall total plant emissions from various plants are probably relatively consistent.

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*See p. I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly production rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will normally operate on the same cycle as the process. Therefore, from the standpoint of cost effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Table IV-1. Total Uncontrolled[a] VOC Emissions[b] from Model Plant for Air-Oxidation Process

Source	Stream Designation (Fig.III-1)	Emissions	
		Ratio (g/kg)[c]	Rate (kg/hr)
Main process vent	A	59.6	1544
Stripper purge vent	B	4.0	104
Fugitive	C	0.42	10.8
Storage and handling	D	2.6	68
Secondary	E	0.0116	0.3
Total		66.6	1727

[a] Uncontrolled emissions are emissions from process for which there are no control devices other than those necessary for economical operation.

[b] Emissions include ethylene oxide, ethylene, and ethane.

[c] g of emissions per kg of ethylene oxide produced.

a. Main Process Vent -- The main process vent (Vent A, Fig. III-1) is the largest process emission source. It contains the nitrogen and unreacted oxygen from the air fed to the reactor, ethane and unreacted ethylene from the ethylene feed, and product EO and by-product CO_2. The composition of this stream, given in Table IV-2, for the model plant depends on the catalyst and the reactor conditions, ethylene feed purity, number of purge reaction stages, and absorber operating conditions.

During startup of a reactor the air feed rate is brought up slowly in correlation with the ethylene feed.[1] Emission ratios during startup are essentially the same as those for normal operation.[2] Process upsets, such as the loss of the stripper feed compressor, can cause a sharp emission increase. When an upset occurs, the ethylene feed is cut back, which reduces the VOC level exhausted from the reactor.[3] The vent can also be directed to an emergency flare.[4]

b. Stripper Purge Vent -- The overhead stream from the stripper column is vented through the stripper purge vent (Vent B, Fig. III-1). The stream is composed of the inert gases and ethylene that become dissolved in the main and purge absorber waters during the recovery of EO from the reaction gases. Normally, any EO that this stream may contain is scrubbed out with water and returned to the process. Table IV-3 gives the composition of this stream for the model plant after EO has been scrubbed out. The emissions from the vent are not affected by process startups or shutdowns.[2] Since the emission is a function of gas solubilities in the circulating water, the water rate used has an effect on the emission.

c. Fugitive Emissions -- Process pumps, compressors, and valves are potential sources of fugitive emissions (Source C, Fig. III-1). The model plant is estimated to have 10 pumps, 2 compressors, and 400 valves handling VOC. The factors in Appendix C were used to determine the emission contribution of these equipment components. The process water from the desorber bottoms is also a potential source of fugitive emissions. The water is recycled through an atmospheric cooling tower, with the excess discharged to wastewater treatment. For the model plant 2500 kg of glycols and aldehydes is recycled per hour in this stream. It is estimated that 0.15%, or 3.8 kg/hr, is lost as VOC to the atmosphere.

Table IV-2. Gas Composition of Main Process Vent in Air-Oxidation-Process Model Plant[a]

Component	Composition (wt %)	Emission Ratio[b] (g/kg)
Ethylene oxide	0.02	1.0
Ethylene	0.80	52.6
Ethane	0.09	6.0
Total VOC	0.91	59.6
Nitrogen	80.23	5253
Oxygen	3.07	201
Carbon dioxide	15.65	1025
Water	0.15	10
Total	100	6548

[a] See refs. 1--3.

[b] g of emission per kg of ethylene oxide produced.

Table IV-3. Gas Composition of Stripper Purge Vent in Air-Oxidation-Process Model Plant[a]

Component	Composition (wt %)	Emission Ratio[b] (g/kg)
Ethylene	3.30	4.0
Nitrogen	13.1	16
Oxygen	1.7	2
Carbon dioxide	81.9	100
Total	100	122

[a] See refs. 1--3.

[b] g of emission per kg of ethylene oxide produced.

d. Storage and Handling Emissions -- Emissions result from the storage and handling of EO, Source D, Fig. III-1. For the model plant EO is stored at 10°C under a nitrogen pad in pressure tanks. For production that is not used captively, shipment is by tank car. Storage tank conditions for the model plant are given in Table IV-4. The uncontrolled storage emissions in Table IV-1 were calculated by assuming that the day tanks are vapor balanced with the storage tanks and that an equivalent amount of vapor, saturated with EO at 10°C, is displaced from the system for each volume of EO produced. Tank car loading losses were calculated similarly, but it was estimated that only 20% of EO production is shipped and that the average handling temperature is 16°C.

Storage and handling practices of an individual plant can vary widely from the model-plant conditions; for instance, some producers store at refrigerated temperatures and near-ambient pressures, whereas others store at ambient temperatures and elevated pressures. Also, the amount shipped, if any, will depend on the individual producer's situation.

e. Secondary Emissions -- Secondary VOC emissions can result from the handling and disposal of process waste streams. For the model plant two potential sources are indicated on the flow diagram (Sources E, Fig. III-1): the heavy ends from the refiner column and the spent catalyst from the reactors.

The refiner heavy ends for the model plant are estimated to be 115-kg/hr total organic containing 6-kg/hr VOC.[5] The VOC emitted to the atmosphere is estimated to be 5%. The spent catalyst is purged before removal, is changed infrequently, and is reclaimed off-site. The potential for emissions from this source is slight.

B. OXYGEN-OXIDATION PROCESS

1. Model Plant

The model plant for this study has an EO capacity of 136 Gg/yr, a typical industrial capacity; this value is based on 8760 hr of operation annually. The model oxygen-oxidation process in Fig. III-2 reflects today's manufacturing and engineering technology. Single process trains with multiple parallel reactors

Table IV-4. Storage Tank Data for Air-Oxidation-Process Model Plant

Parameter	Tank	
	Day	Storage
Contents	EO	EO
No. of tanks required	2	6
Tank size (m^3)	225	470
Turnovers per year	550	89
Bulk temperature (°C)	10	10

are typical. Characteristics of the model plant important to air dispersion are shown in Table B-2 in Appendix B.

2. Sources and Emissions

Sources and emission rates for the oxygen-oxidation process are summarized in Table IV-5. They are meant to represent the typical emissions for the model process; actual emissions of a plant could vary widely for an individual source, but the overall total plant emissions from various plants are probably relatively consistent.

a. CO_2 Purge Vent -- The overhead stream from the reactivator column is vented through the CO_2 purge vent (Vent A, Fig. III-2). The column reactivates the CO_2 absorbent medium for recycle by stripping it of carbon dioxide. The vent emissions consist of most of the by-product CO_2 formed in the reactors, together with some of the ethane from the ethylene feed. The composition of this stream, given in Table IV-6, for the model plant depends mainly on the CO_2 absorbent medium used and the CO_2 absorber operating conditions. The emissions from this source normally are not affected by process startups or shutdowns.

b. Argon Purge Vent -- A discard stream from the reaction recycle gases is vented through the argon purge vent (Vent B, Fig. III-2). The stream contains most of the argon and nitrogen that enter with the oxygen feed and the ethane that enters with the ethylene feed. The composition of this stream (see Table IV-7) for the model plant depends on the argon level that can be tolerated in the reaction system. Argon has a low specific heat compared to other gases, and too high a concentration can affect the reactor temperature control. The quantity vented is directly related to the composition of the oxygen feed. For the process variation in which methane is added to the reactor feed stream the emissions from the vent will also contain methane.

Process upsets and shutdowns normally do not affect this emission source, nor do startups, provided that the oxygen feed composition is established before startup.[1]

c. Stripper Purge Vent -- The overhead stream from the stripper column is vented through the stripper purge vent (Vent C, Fig. III-2), and is composed of the

Table IV-5. Total Uncontrolled[a] VOC Emissions[b] from Model Plant for Oxygen-Oxidation Process

Source	Stream Designation (Fig.III-2)	Emissions Ratio (g/kg)[c]	Emissions Rate (kg/hr)
CO_2 purge vent	A	4.0	62
Argon purge vent	B	10.9	170
Stripper purge vent	C	2.8	44
Fugitive	D	0.55	8.7
Storage and handling	E	2.6	41
Secondary	F	0.013	0.2
		20.9	326

[a] Uncontrolled emissions are emissions from process for which there are no control devices other than those necessary for economical operation.

[b] Emissions include ethylene oxide, ethylene, and ethane.

[c] g of emissions per kg of ethylene oxide produced.

Table IV-6. Gas Composition of CO_2 Purge Vent in Oxygen-Oxidation-Process Model Plant[a]

Component	Composition (wt %)	Emission Ratio[b] (g/kg)
Ethylene	0.23	3.3
Ethane	0.05	0.66
Total VOC	0.28	4.0
Oxygen	0.01	0.10
Carbon dioxide	46.16	666
Water	53.55	773
Total	100	1443

[a] See refs. 3--5.

[b] g of emissions per kg of ethylene oxide produced.

Table IV-7. Gas Composition of Argon Purge Vent in Oxygen-Oxidation-Process Model Plant[a]

Component	Composition (wt %)	Emission Ratio[b] (g/kg)
Ethylene	21.3	8.8
Ethane	5.1	2.1
Total VOC	26.4	10.9
Nitrogen	16.6	7.7
Oxygen	6.4	2.6
Carbon dioxide	31.2	12.9
Argon	18.4	7.7
Water	1.0	0.42
Total	100	42

[a] See refs 3 and 4.

[b] g of emission per kg of ethylene oxide produced.

inert gases and ethylene that become dissolved in the main absorber water during the recovery of EO from the reaction gases. Normally, any EO that this stream may contain is scrubbed out with water and returned to the process. The composition of this stream after the EO is scrubbed is given in Table IV-8. The emission is not affected by process startups or shutdowns.[2] Since the emission is a function of gas solubilities in the circulating water, the water rate used has an effect on the emission.

d. Fugitive Emissions -- Process pumps, compressors, and valves are potential sources of fugitive emissions (Source D, Fig. III-2). The model plant is estimated to have 10 pumps, 2 compressors, and 400 valves handling VOC. The factors in Appendix C were used to determine the emission contribution of these equipment components. The process water from the desorber bottoms is also a potential source of fugitive emissions. The water is recycled through an atmospheric cooling tower, with the excess discharged to wastewater treatment. For the model plant 1100 kg of glycols and aldehydes is recycled in this stream per hour. It is estimated that 0.15%, or 1.7 kg/hr, is lost as VOC to the atmosphere.

e. Storage and Handling Emissions -- Emissions result from the storage and handling of EO, Source D, Fig. III-2. For the model plant EO is stored at 10°C under a nitrogen pad in pressure tanks. For production that is not used captively, shipment is by tank car. Storage tank conditions for the model plant are given in Table IV-9. The uncontrolled storage emissions in Table IV-6 were calculated by assuming that the day tanks are vapor balanced with the storage tanks and that an equivalent amount of vapor, saturated with EO at 10°C, is displaced from the system for each volume of EO produced. Tank car loading losses were calculated similarly, but it was assumed that only 20% of EO production is shipped and that the average handling temperature is 16°C.

Storage and handling practices of an individual plant can vary widely from the model-plant conditions; for instance, some producers store at refrigerated temperatures and near-ambient pressures, whereas others store at ambient temperature and elevated pressures. Also, the amount shipped, if any, will depend on the individual producer's situation.

Table IV-8. Gas Composition of Stripper Purge Vent in Oxygen-Oxidation-Process Model Plant[a]

Component	Composition (wt %)	Emission Ratio[b] (g/kg)
Ethylene	34.2	2.8
Ethane	0.2	0.019
Total VOC	34.4	2.8
Nitrogen	12.2	1.0
Oxygen	8.2	0.67
Carbon dioxide	16.6	1.4
Water	28.6	2.3
Total	100	8.2

[a] See ref 4.

[b] g of emission per kg of ethylene oxide produced.

Table IV-9. Storage Tank Data for Oxygen-Oxidation-Process Model Plant

Parameter	Tank	
	Day	Storage
Contents	EO	EO
No. of tanks required	3	5
Tank size (m^3)	150	470
Turnovers per year	330	64
Bulk temperature (°C)	10	10

The refiner heavy ends for the model plant are estimated to be 70-kg/hr total organic containing 4-kg/hr VOC.[4,5] The VOC emitted to the atmosphere is estimated to be 5%. The spent catalyst is purged before removal, is changed infrequently, and is reclaimed off-site. The potential for emissions from this source is slight.

C. REFERENCES*

1. M. Gans and B. J. Ozero, "For EO: Air or Oxygen?" *Hydrocarbon Processing* *55*(3), 73--77 (1976).

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V. APPLICABLE CONTROL SYSTEMS

A. AIR-OXIDATION PROCESS

1. Main Process Vent

The stream from the main process vent is the largest process emission source (Vent A, Fig. III-1) in the model plant. Control by catalytic oxidation and by thermal oxidation will be evaluated for this source. Although only catalytic oxidation is currently being used for this source, thermal oxidation has the potential for higher efficiency operation, and is used on similar waste streams in other chemical production processes.

a. Catalytic Oxidation -- A catalytic oxidation unit normally consists of a preheater, a catalyst bed, a heat recovery unit, and a stack, together with the necessary controls, blowers, and supplemental fuel supply. In a modern ethylene oxide plant, a catalytic oxidation unit can play a key role in the energy engineering of the plant. It can be an integral part of the system that recovers energy from the process off-gases by use of turbines for compression of the process air feed.[1]

Modern catalytic oxidation units designed for this service can reduce the average effluent ethylene concentration to less than 500 ppm, and probably to as low as 200 ppm. Ethane is more difficult to burn than ethylene, because it has a higher ignition temperature. The ethane effluent concentration will be in the range of twice that of ethylene. The difference in their burning characteristics requires that the ethylene-to-ethane ratio in the feed be controlled to ensure ethane ignition. This limits the amount of ethane that can be burned so as not to exceed the temperature limitation of the catalyst. It has been stated that the next generation of catalytic oxidation units being developed may have the potential to reduce effluent concentrations to the range of 60 ppm.[1]

For the model plant, based on the present modern technology, VOC removal efficiency of 95% is used for the main process vent. The controlled emission is shown in Table V-1.

Table V-1. VOC Controlled Emissions for Air-Oxidation-Process Model Plant

Source	Stream Designation (Fig.III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Emissions	
				Ratio[a] (g/kg)	Rate (kg/hr)
Main process vent	A	Catalytic oxidation	95	3.0	77
		Thermal oxidation	99	0.6	15
Stripper purge vent	B	Compression and recycle	97.3	0.11	2.8
		Catalytic oxidation	95	0.20	5.2
		Thermal oxidation	99	0.040	1.0
Fugitive	C	Detection and correction of major leaks	50	0.21	5.4
Storage and handling	D	Aqueous scrubber	99.5	0.013	0.34
Secondary	E	None		0.012	0.3
Total[b]				3.3	85.8

[a] g of emission per kg of ethylene oxide produced.

[b] Based on catalytic oxidation for the main process vent and compression and recycle for the stripper purge vent.

b. Thermal Oxidation -- A direct-fired thermal oxidation unit for the main process vent would have a combustion chamber that provides sufficient residence time for complete combustion, a supplementary fuel burner that provides auxiliary heat to raise the fume temperatures sufficiently for complete combustion, and provision for good mixing of the fumes with the combustion gases, together with the necessary controls, blower, and stack. A heat recovery system to preheat the feed or generate steam could also be incorporated.

Based on similar incineration applications it is concluded that a properly designed and operated incinerator for this service will achieve a VOC removal efficiency of greater than 99%. An incineration temerature of 870°C and a retention time of 0.5 sec is specified to ensure complete combustion of the waste VOC. While it is possible that greater than 99% VOC removal efficiency could be obtained at lower temperatures, it cannot be predicted dependably.[2]

For the model plant a main process vent removal efficiency of 99% is projected. The controlled emission is shown in Table V-1.

2. Stripper Purge Vent

Two methods of handling the stream from the stripper purge vent (Vent B, Fig. III-1) will be evaluated: compression and recycle to the process and oxidation in the main-process-vent control. Of these two controls, only the recycle option is in present use; another control that has been practiced is burning the stream in a boiler fire box.[1]

a. Compression and Recycle -- In this option the stream is compressed and returned to the purge reactor. When the carbon dioxide contained in the stream is reinjected into the reaction cycle, it can cause impairment of the ethylene selectivity and tend to offset the recovered ethylene value. The reinjected inert gases, plus any incremental increase in VOC due to a lower selectivity, are eventually discharged through the main process vent.

With the recycle ethylene stream assumed to have the same conversion as the main process stream in the purge reactor, the ethylene use efficiency for the model plant is 46%. The net overall VOC emission removal efficiency is 97.3% if the main-process-vent control is catalytic oxidation, and is 99.4% if the control is thermal oxidation (see Table V-1).

b. Stripper Purge Vent Combined with Main Process Vent -- In this option the stream is combined with the larger main-process-vent stream and fed to its control device. If the main-process-vent control is a catalytic oxidation unit that is located in the process so as to recover energy, a compressor would be required to compress the gas to the operating pressure. Under this condition it probably is best to consider only the compression and recycle option because in that option some ethylene value can be recovered.

The VOC reduction efficiency will be the same as for the main process vent, 95% for catalytic oxidation and 99% for thermal oxidation (see Table V-1).

3. Fugitive-Emissions

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry are discussed in a separate EPA document.[3] Emissions from pumps, process valves, and pressure-relief devices can be controlled by an appropriate leak-detection system and with repair and maintenance as needed. Controlled fugitive emissions were calculated with the appropriate factors given in Appendix C and are included in Table V-1.

There are measures that are taken in some EO plants[1] for safety reasons that are also effective in reducing fugitive emissions; for example:

a. using trategic location of hazardous vapor detectors in the plant area to detect EO leaks,
b. equipping EO pumps with double mechanical seals having liquid buffer zones and alarms to indicate a failure of either seal,
c. using pressurized nitrogen in labyrinth shaft seals of centrifugal EO compressors to prevent leakage to the atmosphere,
d. using leak detectors for critical flanges in EO piping,
e. paying extra attention to the maintenance of EO piping because of the danger of fires from leaks.
f. collecting EO leakage or drainage from sampling operations and pump vents, absorbing in water, and then discharging to the sewer.

4. Storage and Handling Sources

It is important to control the EO vapors in the storage and handling areas, Source D, Fig. III-1, because of health and safety hazards. The displaced vapors from the filling of storage tanks and tank cars can be controlled by use of an aqueous scrubber.[1,4] A flare has also been indicated as being used for this service.[5]

An aqueous scrubber is usually a packed tower fed with process water, and the effluent is processed in the plant desorption unit for EO recovery. EO removal efficiency is essentially complete. A VOC removal efficiency of 99.5% for total VOC is used for the controlled emission in Table V-1.

A flare for an EO plant would normally be designed for process emergency venting conditions. If storage and handling emissions were disposed to such a flare, caution must be taken because EO requires only an ignition source to cause safety problems. Use of flares as a control device is discussed in a separate EPA document.[6]

5. Secondary Sources

No control system has been identified for the model plant. Control of secondary emissions is discussed in another EPA report.[7]

B. OXYGEN-OXIDATION PROCESS

1. CO_2 Purge Vent

The stream from the CO_2 purge vent (Vent A, Fig. III-2) has a VOC concentration of only 0.28%, the remainder being CO_2 and water. For the model plant this amounts to 62 kg of VOC per hour. Control of this stream by thermal or catalytic oxidation would not be practical; in the model plant it is left uncontrolled (Table V-2).

A theoretical design for controlling this emission that has been proposed[1] consists of two-stage flashing of the CO_2 absorber effluent before it is introduced into the reactivator. The ethylene will tend to flash out preferentially. This flash gas is then compressed and returned to the absorber. A preliminary estimate indicates that a 60% efficiency may be an attainable value for this type of control.

Table V-2. VOC Controlled Emissions for Oxygen-Oxidation-Process Model Plant

Source	Stream Designation (Fig.III-2)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Emissions	
				Ratio[a] (g/kg)	Rate (kg/hr)
CO_2 purge vent	A	None		4.0	62
Argon purge vent	B	Used as fuel	99.9	0.011	0.17
Stripper purge vent	C	Compression and recycle	99.7	0.0084	0.13
Fugitive	D	Detection and correction of major leaks	62	0.21	3.3
Storage and handling	E	Aqueous scrubber	99.5	0.013	0.21
Secondary	F	None		0.013	0.2
Total				4.3	66.0

[a] g of emission per kg of ethylene oxide produced.

One producer[4] uses the CO_2 purge vent in another process. The ultimate fate of the contained VOC is thermal oxidation. When the other process unit is down, the vent emissions are oxidized in an existing incinerator.

2. Argon Purge Vent

The emissions from the argon purge vent (Vent B, Fig. III-2) are high in ethylene and will support combustion. In the process variation in which methane is used in the reactor, this vent stream will also contain appreciable methane, making it an even better fuel gas. The emissions from this vent can be disposed of readily in a fire box or fuel header. At least several producers[1,4,5] do use it as a fuel.

For the model plant the emission control will be to use the gas as fuel (Table V-2). An alternative method of control would be to burn the gas in a flare. The VOC reduction efficiency when the vent gas is burned as fuel can be greater than 99.9%.[6]

3. Stripper Purge Vent

The emissions from the stripper purge vent (Vent C, Fig. III-2) are high in ethylene and will support combustion but may require supplemental fuel for flame stability. In the process variation in which methane is used in the reactor, the emissions will also include some methane. In older processes, this vent emission has been disposed of in a boiler fire box; it also could be flared. In newer installations it is compressed and returned to the reaction cycle in the CO_2 absorber feed.[1]

For the model plant (Table V-2) the emission control evaluated will consist of compression and recycling. This type of control has two negative effects on the process. The reinjected carbon dioxide requires additional energy for its removal via the CO_2 absorption system, and the reinjected argon must be vented in the argon purge vent. The net VOC reduction efficiency is 99.7% when the argon purge vent (Vent B) is used as a fuel gas and the CO_2 purge vent (Vent A) is uncontrolled.

4. Fugitive Emissions

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry are discussed in a separate EPA document.[3] Emissions from pumps, process valves, and pressure-relief devices can be controlled by an appropriate leak-detection system and with repair and maintenance as needed. Controlled fugitive emissions were calculated with the appropriate factors given in Appendix C and are included in Table V-2.

Some measures that are taken in one EO plant[1] for safety reasons are also effective in reducing fugitive emissions; for example:

a. using strategic location of hazardous vapor detectors in the plant area to detect EO leaks,
b. equipping EO pumps with double mechanical seals having liquid buffer zones and alarms to indicate a failure of either seal,
c. using pressurized nitrogen in labyrinth shaft seals of centrifugal EO compressors to prevent leakage to the atmosphere,
d. using leak detectors for critical flanges in EO piping,
e. paying extra attention to the maintenance of EO piping because of the danger of fires from leaks,
f. collecting EO leakage or drainage from sampling operations and pump vents, absorbing in water, and then discharging to the sewer.

5. Storage and Handling Sources

It is important to control the EO vapors in the storage and handling areas, Source E, Fig. III-2, because of health and safety hazards. The displaced vapors from the filling of storage tanks and tank cars can be controlled by use of an aqueous scrubber.[1,4] A flare has also been indicated as being used for this service.[5]

An aqueous scrubber is usually a packed tower fed with process water, and the effluent is processed in the plant desorption unit for EO recovery. EO removal efficiency is essentially complete, and a removal efficiency of 99.5% for total VOC is used for the controlled emission in Table V-2.

A flare for an EO plant would normally be designed for process emergency venting conditions. If storage and handling emissions were disposed to such a flare, caution must be taken because EO requires only an ignition source to cause safety problems. Use of flares as a control device is discussed in a separate EPA document.[6]

6. Secondary Sources

No control system has been identified for the model plant. Control of secondary emissions is discussed in another EPA report.[7]

C. REFERENCES*

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

1. Air-Oxidation Process

Table VI-1 shows the environmental impact of reducing VOC emissions by application of the described control systems (Sect. V) to the model plant. From an energy standpoint a typical uncontrolled air-oxidation-process EO plant will produce a heat surplus of 6 to 11 MJ per kg of EO and will require power of about 5 MJ per kg of EO.[1]

a. Main Process Vent -- Emissions from the main process vent can be controlled by a catalytic oxidizer or a thermal oxidizer with the environmental impacts described below:

Catalytic oxidation -- The catalytic oxidizer reduces VOC emissions by 12.9 Gg/yr for the model plant. It uses supplemental fuel to preheat the waste gas and electrical power for blowers, lighting, and instruments, with a total energy requirement of 2.5 MJ per kg of EO. If heat recovery equipment is installed and approximately 62% of the available energy from the combustion gases is recovered, this would amount to 2.2 MJ per kg of EO, or a net energy usage of 0.3 MJ/kg for the model plant.

Thermal oxidation -- The thermal oxidizer reduces VOC emissions by 13.4 Gg/yr for the model plant.

The thermal oxidizer uses supplemental fuel to heat the waste gas stream and electrical power for blowers, lighting, and instruments. The total energy required is 9.9 MJ per kg of EO produced. If heat recovery equipment is installed and approximately 62% of the available energy from the combustion gases is recovered, this would amount to 8.2 MJ per kg of EO, or a net usage of 1.7 MJ/kg for the model plant.

b. Stripper Purge Vent -- The compression and recycle of the emissions from this vent back to the process, together with a catalytic oxidizer on the main process vent, reduces VOC emissions by 0.9 Gg/yr for the model plant. Electri-

Table VI-1. Environmental Impact of Controlled Air-Oxidation-Process Model Plant

Emission Source	Stream or Vent Designation (Fig. III-1)	Control Device or Technique	VOC Emission Reduction	
			(%)	(Mg/yr)
Main process vent	A	Catalytic oxidation	95	12,850
		Thermal oxidation	99	13,390
Stripper purge vent	B	Compression and recycle	97.3	886
		Catalytic oxidation	95	865
		Thermal oxidation	99	902
Fugitive	C	Detection and correction of major leaks	50	47
Storage and handling	D	Aqueous scrubber	99.5	593
Secondary	E	None		
Total[a]				14,376

[a] Based on catalytic oxidation for the main process vent and compression and recycle for the stripper purge vent.

cal energy, 0.03 MJ per kg of EO produced, is required for compressing this stream, and ethylene equivalent to 1.8 g/kg of EO is recovered.

c. Fugitive Emissions -- The control methods previously described for these emissions are major leak detection and repair of equipment components. Application of these systems results in a VOC reduction of 0.05 Gg/yr for the model plant.

d. Storage and Handling -- The aqueous scrubber reduces VOC emissions from storage and handling by 0.59 Gg/yr and recovers EO equivalent to 2.6 g per kg of EO produced for the model plant. The electrical energy and process water required for the aqueous scrubber system are negligible.

2. Oxygen-Oxidation Process

Table VI-2 shows the environmental impact of reducing VOC emissions by application of the described control systems to the model plant. From an energy standpoint a typical uncontrolled oxygen-oxidation process EO plant will produce a heat surplus of about 9 MJ per kg of EO produced and will require power of 1.5 to 2.5 MJ/kg of EO.[1] This does not include the energy for the oxygen supply plant.

a. Argon Purge Vent -- The use of emissions from this vent as fuel gas will reduce VOC emissions by 1.5 Gg/yr for the model plant, and the heating value will be equal to 0.56 MJ/kg of EO produced.

b. Stripper Purge Vent -- The compression and recycle of the emissions from this vent back to the process, together with use of the argon purge vent emissions as fuel, reduce VOC emissions by 0.4 Gg/yr and recover ethylene equivalent to 1.4 g per kg of EO produced for the model plant. The electrical energy consumption for the compressor per kg of EO produced is relatively small.

c. Fugitive Emissions -- The control methods described for these emissions are major leak detection and repair of equipment components. Application of these systems results in a VOC reduction of 0.05 Gg/yr for the model plant.

Table VI-2. Environmental Impact of Controlled Oxygen-Oxidation-Process Model Plant

Emission Source	Stream or Vent Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	VOC Emission Reduction (Mg/yr)
CO_2 purge vent	A	None		
Argon purge vent	B	Used as fuel	99.9	1488
Stripper purge vent	C	Compression and recycle	99.7	384
Fugitive	D	Detection and correction of major leaks	62	47
Storage and handling	E	Aqueous scrubber	99.5	357
Secondary	F	None		
Total				2276

d. Storage and Handling -- The aqueous scrubber reduces VOC emissions from storage and handling by 0.36 Gg/yr and recovers EO equivalent to 2.6 g per kg of EO produced for the model plant. The electrical energy and process water required for the aqueous scrubber system are negligible.

B. CONTROL COST IMPACT

This section gives estimated costs and cost-effectiveness data for control of VOC emissions resulting from the production of ethylene oxide. Details of the model plant (Figs. III-1 and III-2) are given in Sects. III and IV. Cost estimate sample calculations are included in Appendix D.

Capital cost estimates represent the total investment required for purchase and installation of all equipment and material required for a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of ethylene oxide production lost during installation or startup, research and development, or land acquisition.

Bases for the annual cost estimates for the control alternatives include utilities, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors used are itemized in Table VI-3.

1. Air-Oxidation Process

a. Main-Process Vent (Vent A, Fig. III-1) -- This is the major process emission source. Two emission controls for this vent have been evaluated, a catalytic oxidizer and a thermal oxidizer. Both controls are evaluated with and without heat recovery options. Heat recovery is based on the use of a waste heat boiler on the exit gas. Recuperative recovery could be used to preheat the feed streams and thereby reduce the supplemental fuel requirements. The emission control cost estimates for these systems for the model plant are shown in Table VI-4. The installed capital cost, net annual cost, and cost-effectiveness variations with capacity are shown in Figs. VI-1 to VI-3. See Appendix D for the cost estimate sample calculations for a catalytic oxidizer and a thermal oxidizer, based on complete installations as described in the control device evaluation reports on catalytic oxidation and thermal oxidation.[2,3]

Table VI-3. Annual Cost Parameters

Operating factor	8760 hr/yr[a]
Operating labor	$15/man-hr
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital cost
Capital recovery, 18%[b]	
Taxes, insurances, administration charges, 5%	
Utilities	
Electric power	$8.33/GJ ($0.03/kWh)
Natural gas	$1.90/GJ ($2.00/thousand ft^3 or million Btu)
Heat recovery credits (equivalent to natural gas)	$1.90/GJ ($2.00/million Btu)
Ethylene recovery credit	$0.287/kg

[a] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[b] Based on 10-year life and 12% interest.

Table VI-4. Emission Control Cost Estimates for Model Plants Using Air-Oxidation or Oxygen-Oxidation Process

Emission Source	Control	Total Installed Capital Cost	Annual Operating Costs: Utilities	Man-power	Catalyst Replacement	Fixed Costs	Recovery Credits	(A) Net Annual	(B) Total VOC Emission Reduction: Mg/yr	Percent	(C)[a] Total VOC Cost Effectiveness (per Mg)
				Air-Oxidation Process							
Main process vent (A)[b]	Catalytic oxidizer										
	With waste heat boiler	$2,600,000	$1,170,000	$36,000	$86,000	$754,000	$1,470,000	$ 576,000	12,850	95	$ 45
	Without heat recovery	1,500,000	1,170,000	18,000	86,000	435,000	None	1,709,000	12,850	95	133
	Thermal oxidizer										
	With waste heat boiler	3,100,000	4,310,000	36,000		899,000	3,531,000	1,714,000	13,390	99	128
	Without heat recovery	1,400,000	4,310,000	18,000		406,000	None	4,734,000	13,390	99	354
Stripper purge vent (B)[b]	Compression and recycle	500,000	49,000	5,000		145,000	118,000	81,000	886	97.3[c]	91
				Oxygen-Oxidation Process							
Stripper purge vent (C)[d]	Compression and recycling	55,000	4,000	4,000		16,000	55,000	($31,000)[e]	382	99.7	(81)[e]

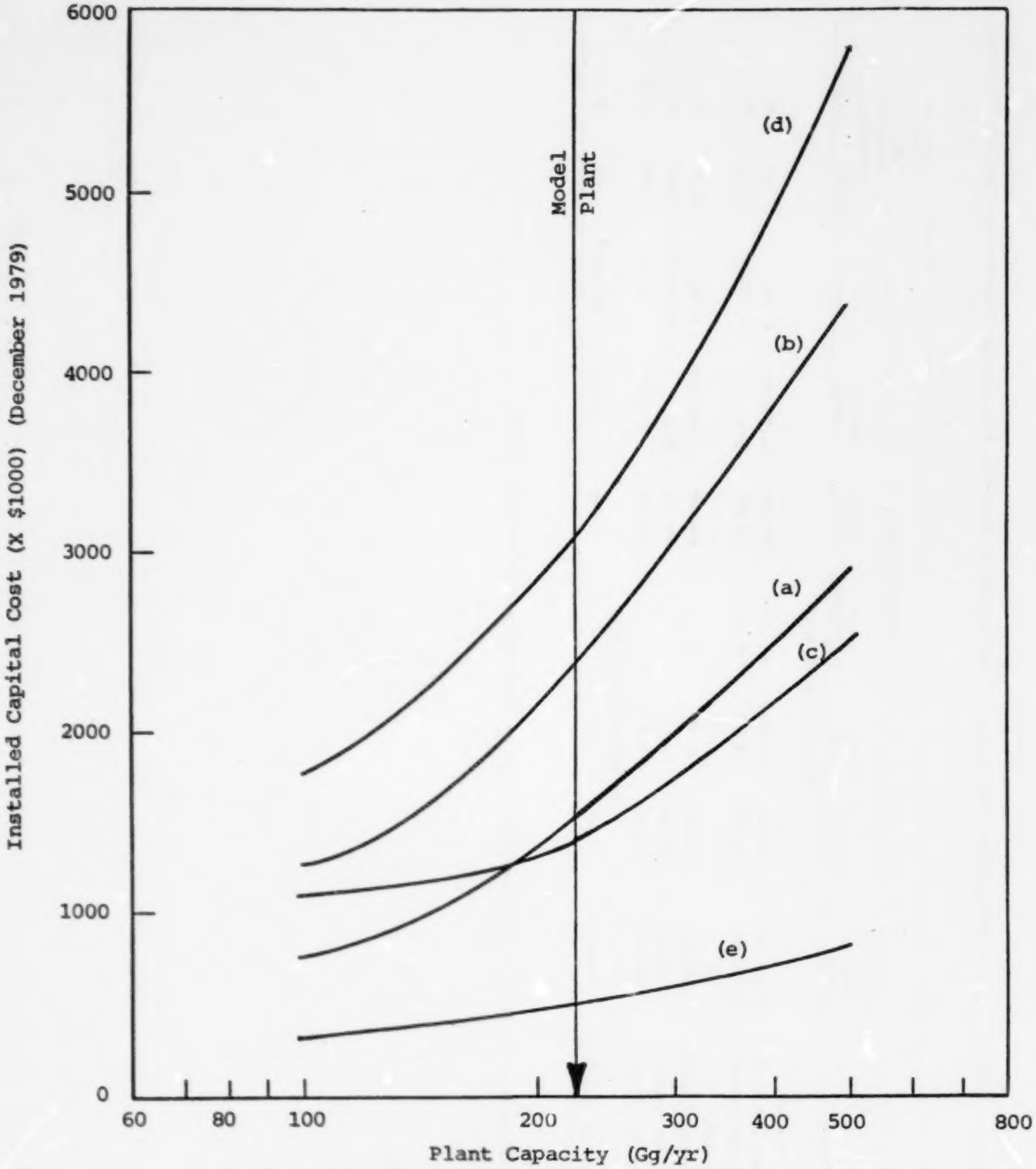
[a] (C) = (A) ÷ (B).

[b] Vent designation shown on Fig. III-1.

[c] Reduction percent is based on 46% VOC reduction in the purge reactor and 95% in the main-process-vent catalytic oxidizer control.

[d] Vent designation shown on Fig. III-2.

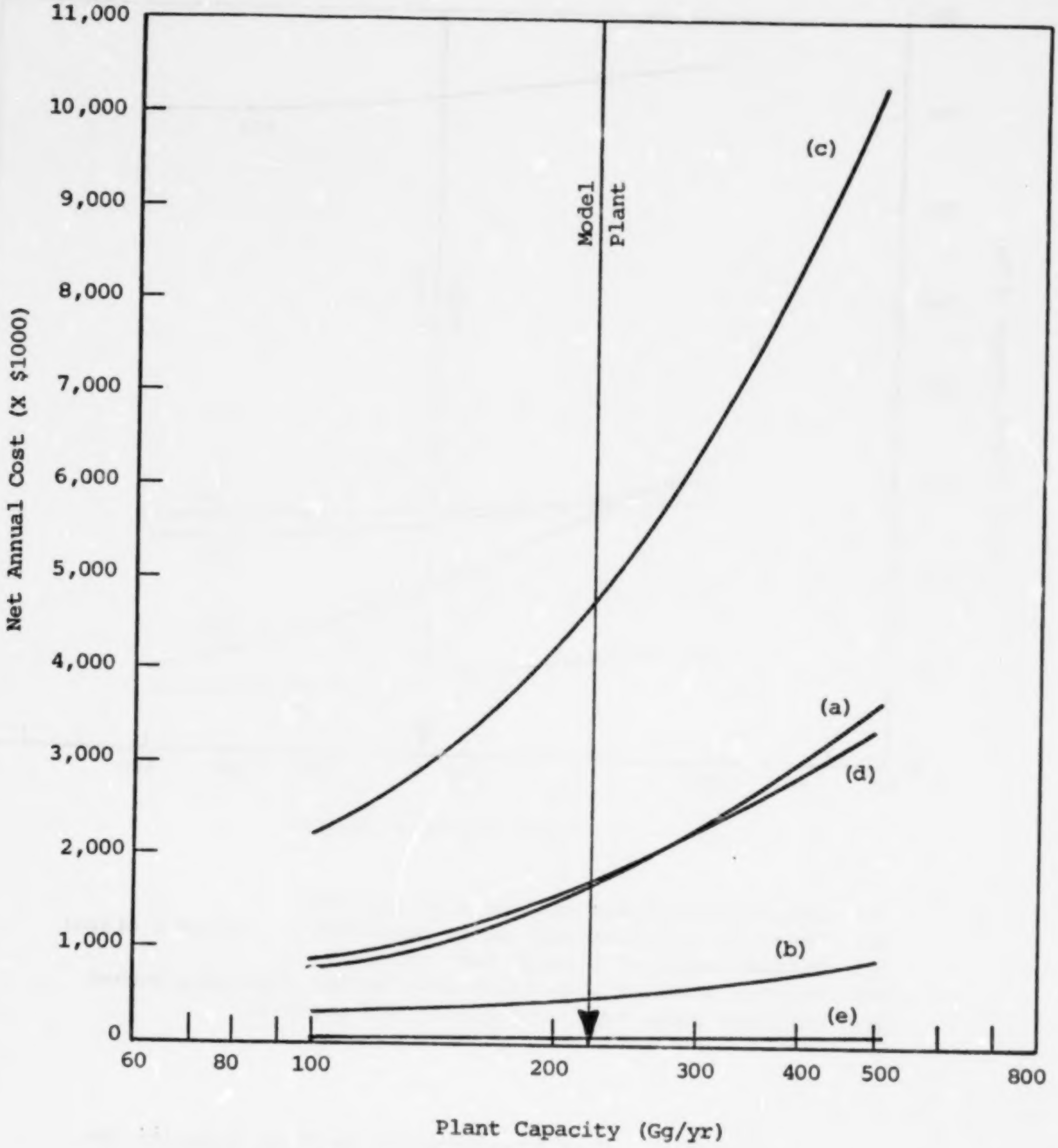
[e] Savings.



(a) Catalytic oxidizer without heat recovery
(b) Catalytic oxidizer with waste heat boiler (100-psig steam)
(c) Thermal oxidizer without heat recovery
(d) Thermal oxidizer with waste heat boiler (250-psig steam)
(e) Stripper purge vent compression and recycle

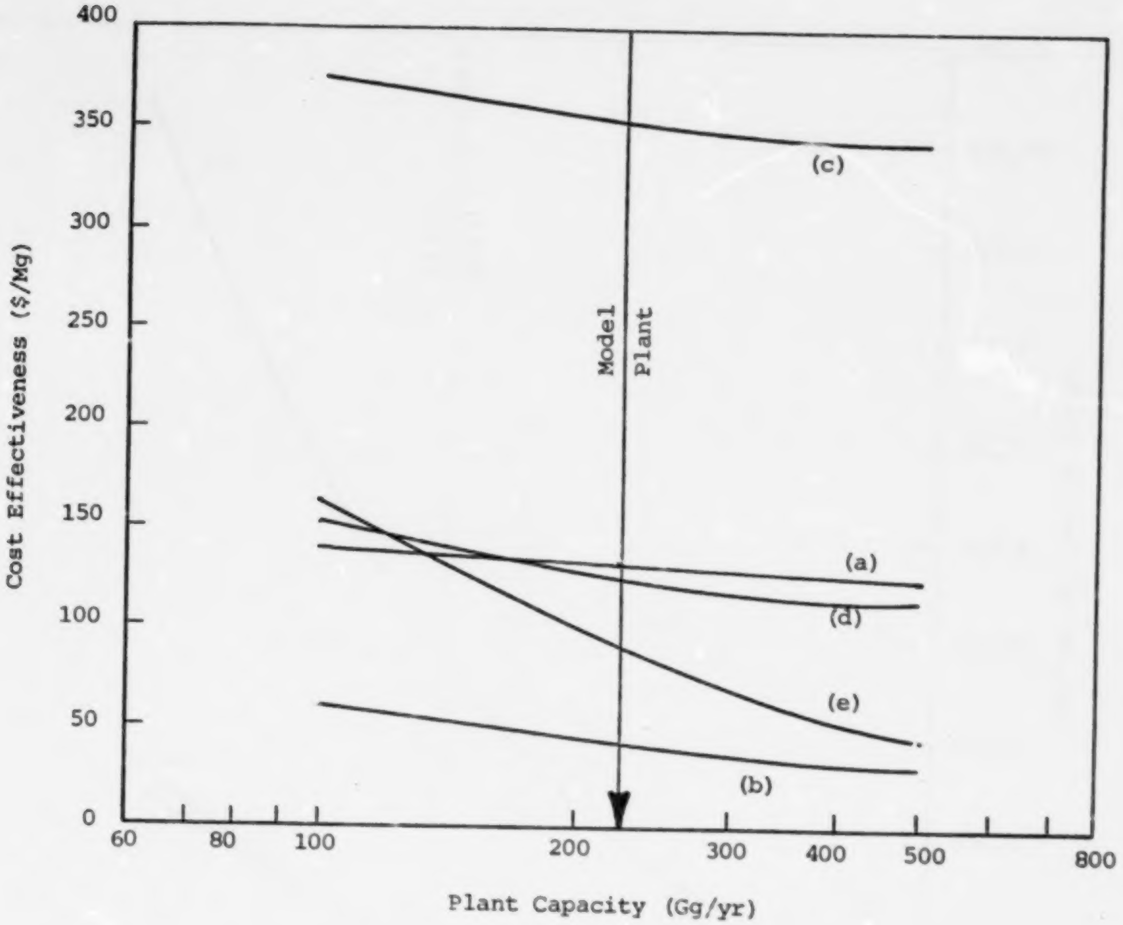
324

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Emission Control for Air-Oxidation Process



(a) Catalytic oxidizer without heat recovery
(b) Catalytic oxidizer with waste heat boiler (100-psig steam)
(c) Thermal oxidizer without heat recovery
(d) Thermal oxidizer with waste heat boiler (250-psig steam)

Fig. VI-2. Net Annual Cost vs Plant Capacity for Emission Control for Air-Oxidation Process



(a) Catalytic oxidizer without heat recovery
(b) Catalytic oxidizer with waste heat boiler (100-psig steam)
(c) Thermal oxidizer without heat recovery
(d) Thermal oxidizer with waste heat boiler (250-psig steam)
(e) Stripper purge vent compression and recycle

Fig. VI-3. Cost Effectiveness vs Plant Capacity for Emission Control for Air-Oxidation Process

b. Stripper Purge Vent (Vent B, Fig. III-1) -- Two control methods for this stream are discussed in Sect. V, compression and recycle to the purge reactor and combining the stream with the main-process-vent stream to its control device. Only the compression and recycle control has been evaluated; the cost estimate for the model plant is shown in Table VI-4. The installed capital cost, net annual cost, and cost-effectiveness variations with capacity are shown in Figs. VI-1 to VI-3. The recovery credits are based on the estimate that 46% of the recycled ethylene is reacted in the purge reactor, and the overall VOC removal efficiency is based on the main process vent being controlled by a catalytic oxidizer with 95% efficiency.

Combining this vent stream with the main-process-vent (Vent A) stream to its control device would increase the VOC load to the control by only about 7%. This incremental increase would not significantly change the cost analysis made in Sect. B.1.a for the main-process-vent control options.

c. Fugitive Sources -- A control system for fugitive sources is defined in Appendix C. Another EPA report covers fugitive emissions and their applicable controls for the synthetic organic chemicals manufacturing industry.[4]

d. Storage and Handling Sources (Vent D, Fig. III-1) -- The system for controlling storage and handling emissions is an aqueous scrubber. Another EPA report covers storage and handling emissions for all the synthetic organic chemicals manufacturing industry.[5]

e. Secondary Sources -- No control system has been defined for secondary emissions from the model plant.

2. Oxygen-Oxidation Process

a. CO_2 Purge Vent (Vent A, Fig. III-2) -- No control system has been defined for this vent in the model plant. A theoretical design for controlling the emissions is discussed in Sect. V, but additional data would be necessary before the emission control cost could be estimated.

b. Argon Purge Vent (Vent B, Fig. III-2) -- The emissions from this vent can be used readily as a fuel gas. The cost to pipe this stream to an existing fire box or to incorporate it into a fuel header system would be very site specific, depending on a particular facility situation. Nevertheless, the cost would be relatively small compared to the fuel value credit for this vent, and there would in many cases be a cost-effectiveness savings.[6]

c. Stripper Purge Vent (Vent C, Fig. III-2) -- One emission control for this source has been evaluated, compression and recycle to the process CO_2 absorber. The emission control cost estimate for the model plant is shown in Table VI-4. The installed capital cost, net annual cost, and cost-effectiveness variations with capacity are shown in Figs. VI-4 to VI-6. The recovery credits are based on an estimate that 50% of the recycled ethylene is reacted. The overall VOC removal efficiency is based on the unreacted ethylene exiting with the argon purge vent (Vent B) and the argon purge used as a fuel gas. Disposal of emissions from this vent directly as a fuel gas or to a flare is also discussed in Sect. V as controls. Disposal as a fuel gas, although comparable in VOC reduction efficiency to compression and recycle, would not be as cost effective because it does not provide for recovery of the contained ethylene value. Flaring this stream would not provide for recovery of ethylene content nor would there be a heat content value.

d. Fugitive Sources -- A control system for fugitive sources is defined in Appendix C. Another EPA report covers fugitive emissions and their applicable controls for the synthetic organic chemicals manufacturing industry.[4]

e. Storage and Handling Sources (Vent D, Fig. III-2) -- The system for controlling storage and handling emissions is an aqueous scrubber. Another EPA report covers storage and handling emissions for all the synthetic organic chemical manufacturing industry.[5]

f. Secondary Sources -- No control system has been defined for secondary emissions from the model plant.

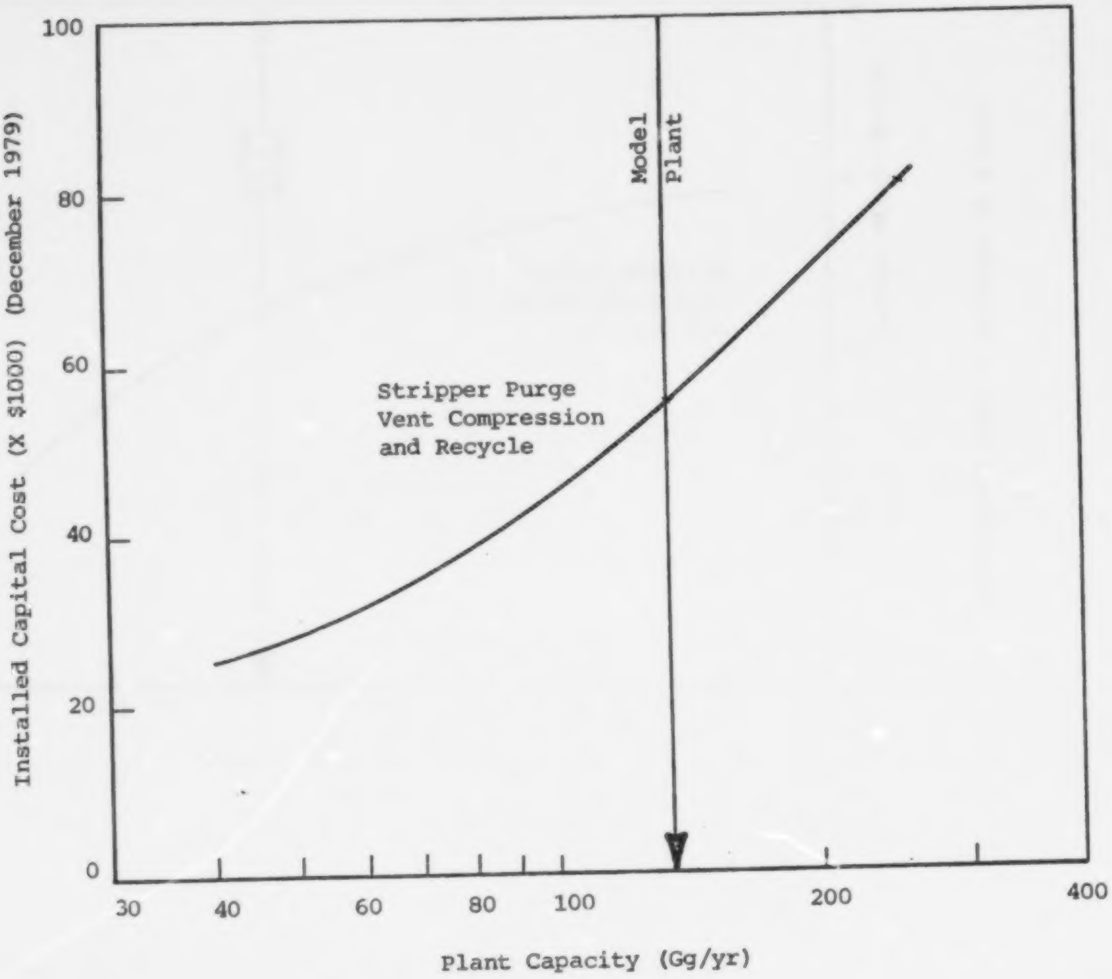


Fig. VI-4. Installed Capital Cost vs Plant Capacity for Emission Controls for Oxygen-Oxidation Process

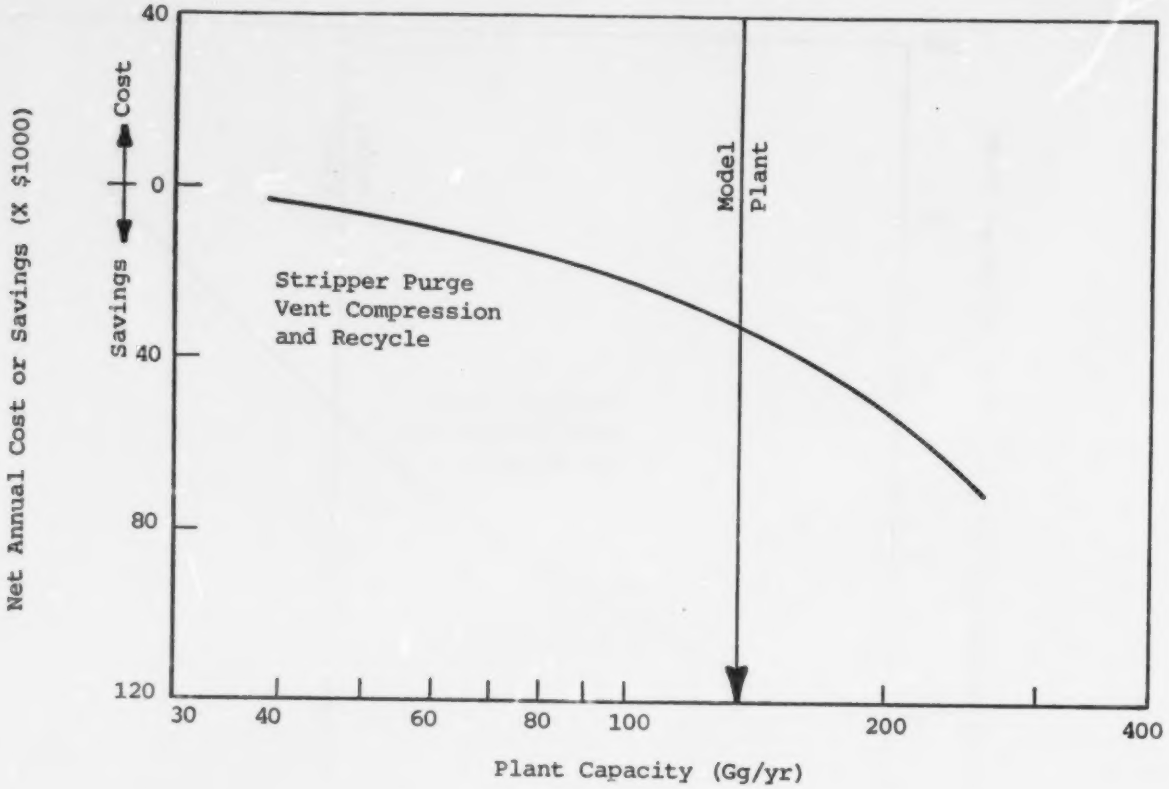


Fig. VI-5. Net Annual Cost or Savings vs Plant Capacity for Emission Controls for Oxygen-Oxidation Process

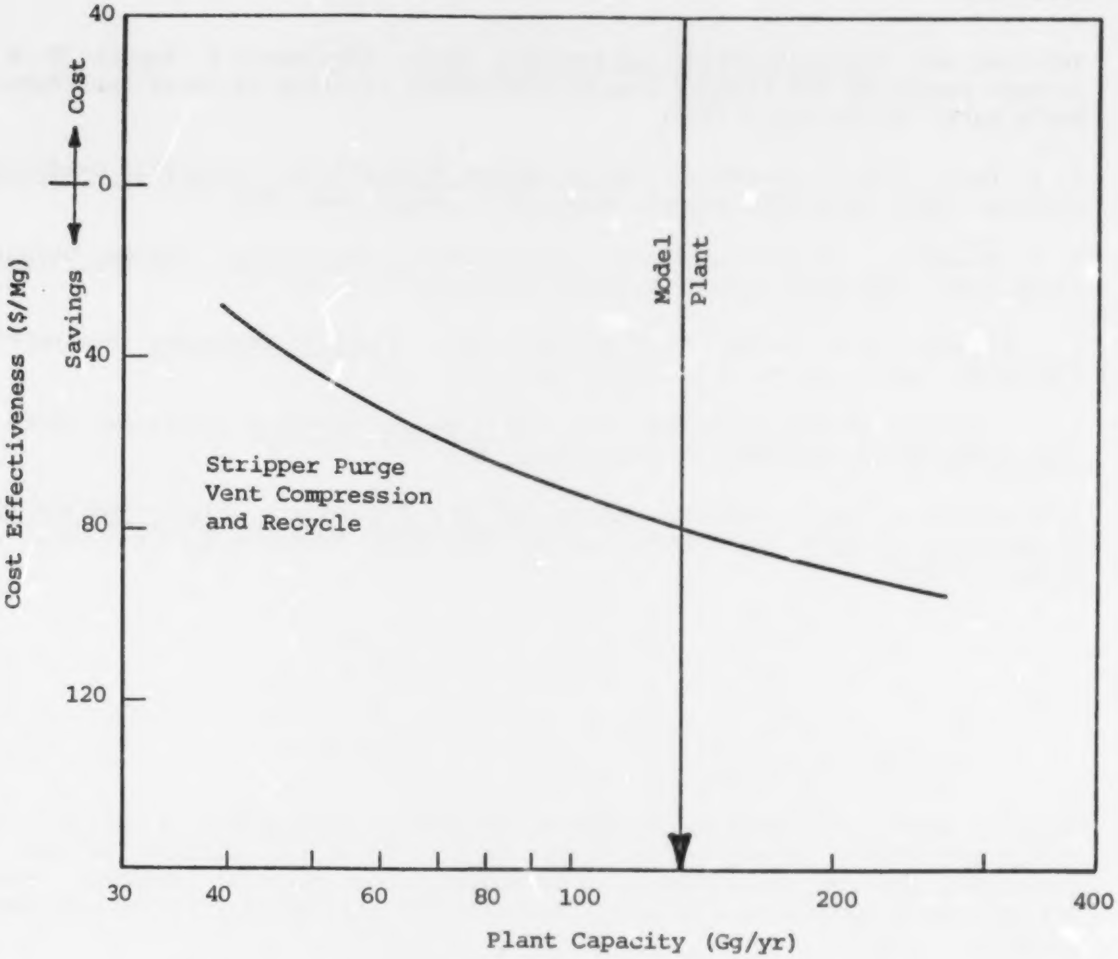


Fig. VI-6. Cost Effectiveness vs Plant Capacity for Emission Controls for Oxygen-Oxidation Process

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*Usually, when a reference is located at the end of a paragraph it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Ethylene oxide (EO) is currently manufactured by one of two processes, air oxidation of ethylene or oxygen oxidation of ethylene. Before 1977 it was also manufactured by the chlorohydrin process, which was the predominant process until 1957. The domestic production capacity, including Puerto Rico, of EO for July 1, 1979, was estimated to be 2783 Gg, with 63% based on the air-oxidation process and 37% on the oxygen-oxidation process. The 1978 industry utilization rate was approximately 82%, with about 70% of EO produced being used in the production of ethylene glycols. The estimated EO consumption annual growth is 4.5 to 5.5%.[1]

Emission sources and uncontrolled and controlled emission rates for the air-oxidation process model plant are given in Table VII-1 and for the oxygen-oxidation process in Table VII-2.

The air-oxidation-process major emission source is the main process vent. Catalytic-oxidation units, located in the process sequence to maximize energy recovery, are used as controls for this vent. Present catalytic-oxidation technology can give a 95% VOC reduction efficiency, which may be improved by a new generation of technology.[2] Thermal oxidation could be used to control this vent with an estimated 99% efficiency but is not as cost effective and may not fit as well as catalytic oxidation into the overall process energy recovery design.

The oxygen-oxidation-process major emission that is not controlled is the CO_2 purge vent, which emits a dilute VOC stream consisting mainly of CO_2 and water vapor. A theoretical design consisting of a process change in regenerating the CO_2 absorbing fluid has been proposed as a potential method for reduction of the VOC content,[2] but it would require development and its practical removal efficiency may be only about 60%. The other major emission is from the argon purge vent, but this stream can readily be used as a fuel gas.

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[1] S. A. Cogswell, "Ethylene Oxide," pp. 654.5031A—654.5033F in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1980).

[2] J. F. Lawson, IT Enviroscience, Trip Report for Visit to Union Carbide Corp., South Charleston, WV, Dec. 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

Table VII-1. Emission Summary for Air-Oxidation-Process Model Plant (227,000 Mg/yr)

Emission Source	Stream Designation (Fig.III-1)	VOC Emission Rate (kg/hr) Uncontrolled	VOC Emission Rate (kg/hr) Controlled
Main process vent	A	1544	77[a]
Stripper purge vent	B	104	2.8[b]
Fugitive	C	10.8	5.4
Storage and handling	D	68	0.34
Secondary	E	0.3	0.3
Total		1727	85.8

[a] Based on catalytic oxidation as the control.

[b] Based on compression and recycle to the process as the control.

Table VII-2. Emission Summary for Oxygen-Oxidation-Process Model Plant (136,100 Mg/yr)

Emission Source	Stream Designation (Fig.III-2)	VOC Emission Rate (kg/hr) Uncontrolled	VOC Emission Rate (kg/hr) Controlled
CO_2 purge vent	A	62	62
Argon purge vent	B	170	0.17
Stripper purge vent	C	44	0.13
Fugitive	D	8.7	3.3
Storage and handling	E	41	0.21
Secondary	F	0.2	0.2
Total		326	66.0

The emissions from the stripper purge vent in both processes are readily controlled by being compressed and recycled to an appropriate place in the process. Storage and handling vent streams can be scrubbed for EO recovery and recycled back to the process. Potential secondary emissions are minor.

APPENDIX A

Table A-1. Properties of Ethylene*

Synonyms	Acetene, ethene
Molecular formula	C_2H_4
Molecular weight	28.06
Physical state	Gas
Vapor pressure	456 mPa at 0°C
Vapor density	0.98
Boiling point	-103.9°C at 760 mm Hg
Melting point	-169°C
Density	0.99267 at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan *et al*., "Ethylene Oxide," p. AII-260 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals D-E)*, Rev. 1, Appendix A, MTR-7248, MITRE Corp., McLean, VA (September 1976).

APPENDIX B

Table B-1. Air-Dispersion Parameters for Air-Oxidation-Process Model Plant with a Capacity of 227,000 Mg/yr

Source	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Uncontrolled Emissions						
Main process vent	429	17	0.6	310	37.5	132.5
Stripper purge vent	28.9	30	0.1	320	0.6	76.5
Fugitive emissions*	3.0			295		
Storage and handling (6 spheres, 2 horizontal tanks)	18.9	9.7	9.7	283		
Secondary emissions	0.083			295		
Controlled Emissions						
Main process vent						
Catalytic oxidizer	21.4	15	3	530	76.8	10.9
Thermal oxidizer	4.2	15	3	530	84.9	12.0
Stripper purge vent (with main process vent)	0.8					
Fugitive emissions*	1.5			295		
Storage and handling	0.09	18	0.1	310	0.01	1.3

*Fugitive emissions are distributed over a rectangular area of 100 m X 400 m.

Table B-2. Air-Dispersion Parameters for Oxygen-Oxidation-Process Model Plant with a Capacity of 136,100 Mg/yr

Source	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled Emissions			
CO_2 purge vent	17.2	20	0.3	375	6.0	84.2
Argon purge vent	47.2	20	0.3	310	0.13	1.8
Stripper purge vent	12.2	20	0.1	310	0.025	3.2
Fugitive emissions[a]	2.4			295		
Storage and handling (5 spheres, 3 horizontal tanks)	11.4	9.7	9.7	283		
Secondary emissions	0.056			295		
			Controlled Emissions			
Argon purge vent[b]	0.05					
Stripper purge vent[b]	0.04					
Fugitive emissions[a]	0.92					
Storage and handling	0.06	18	0.1	310	0.006	0.8

[a] Fugitive emissions are distributed over a rectangular area of 100 m X 300 m.

[b] Vents used as fuel gas.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST ESTIMATE DETAILS

This appendix contains sample calculations showing how the costs presented in this report were estimated.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure D-1 illustrates this relationship. The contingency allowance indicated is included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. D-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternate within the limits of accuracy indicated.

A. MAIN-PROCESS VENT——AIR-OXIDATION PROCESS

To determine the cost estimates for controlling the vent emissions from the air-oxidation process main-process vent (Vent A, Fig. III-1), emission flow details for the model plant were taken from Tables IV-1 and IV-2 and the waste-gas flow calculated as shown in Table D-1:

10,859 lb-moles/hr X 359 scf/lb-mole ÷ 60 min/hr = 65,000 scfm of waste gas.

Multiplying the VOC components by their heating value and dividing by the SCF of waste gas gives the heating value:

$$\frac{(337 \text{ X } 22{,}170 + 2992 \text{ X } 21{,}770 + 75 \text{ X } 12{,}630)}{60} \div 65{,}000 = 19 \text{ Btu/scf of waste gas.}$$

The waste-gas flows of EO plants larger and smaller than the model plant were estimated by direct ratio to the model plant:

100-Gg/yr plant = 100/227 X 65,000 = 29,000 scfm of waste gas.

500-Gg/yr plant = 500/227 X 65,000 = 143,000 scfm of waste gas.

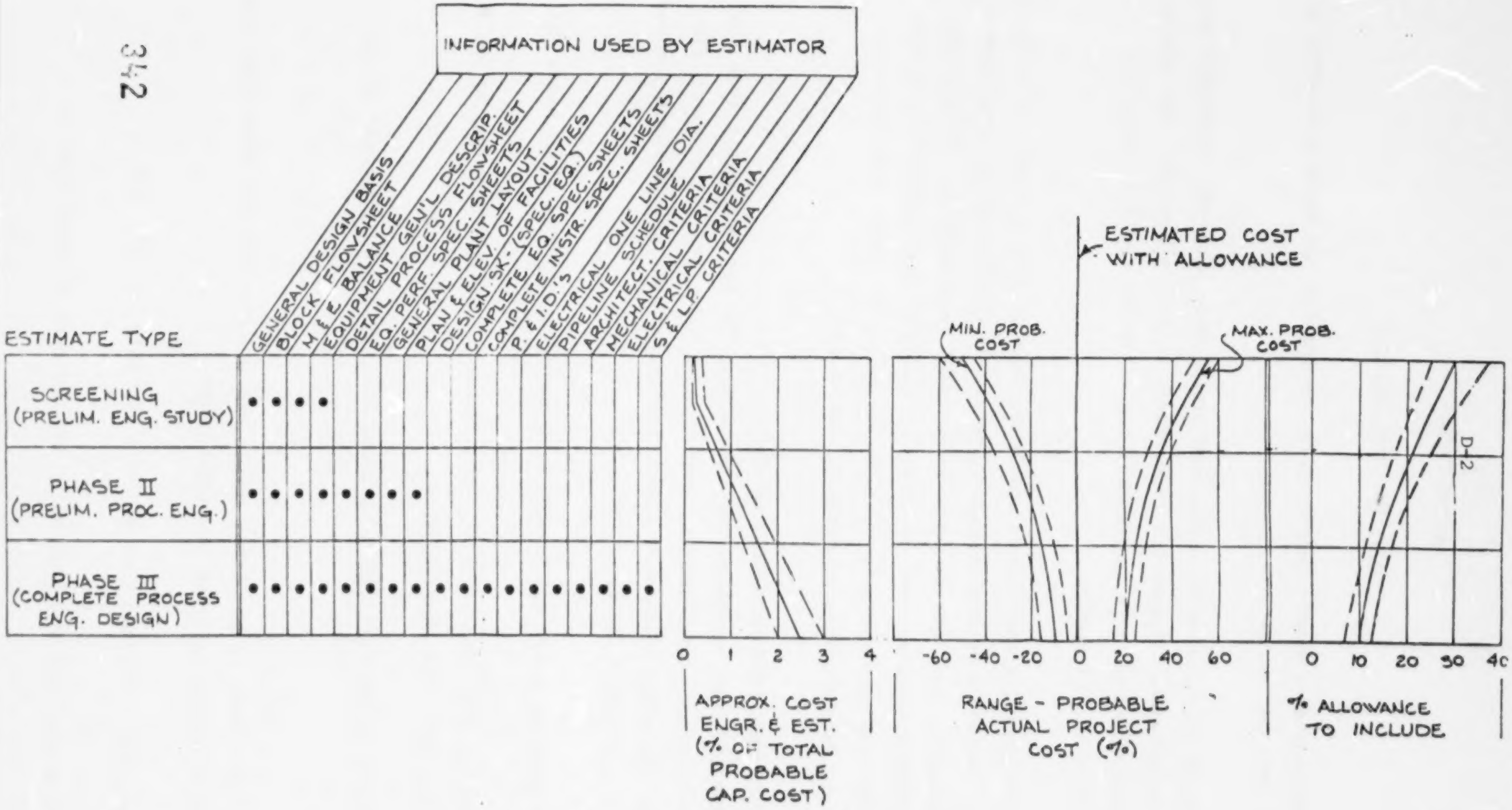

Fig. D-1. Precision of Capital Cost Estimates

LATEST REVISION - 5/2/77

Table D-1. Emission Flow Data

			Flow Rate			
Component	(A) Molecular Weight	Weight Percent	(kg/hr)	(lb/hr)	(B) Adjusted (lb/hr)[a]	(C) (lb-moles/hr)[b]
Ethane	30	0.09	153	337	337	11
Ethylene	28	0.80	1,357	2,992	2,992	107
EO	44	0.02	34	75	75	2
N_2	28	80.22	136,110	300,071	262,593	9,378
O_2		3.07	5,209	11,484		
CO_2	44	15.65	26,553	58,539	58,539	1,330
H_2O	18	0.15	255	562	562	31
Total		100	169,671	374,060	325,098	10,859

[a] Adjusted to a no-oxygen basis by deducting 3.26 lb of N_2 per lb of oxygen, as well as deducting the contained oxygen.

[b] (B) ÷ (A) = (C).

1. Catalytic Oxidizer

The costs given in Table D-2 were developed from the control device evaluation report.[1]

2. Thermal Oxidizer

The costs given in Table D-3 were developed from the control device evaluation report.[2] In Sect. V-A.1.b of this report the stated oxidation conditions are 870°C (1600°F) and 0.5-sec residence time for 99% destruction.

B. STRIPPER PURGE VENT——AIR-OXIDATION PROCESS

For the model plant it was calculated that a 250-hp compressor handling 1100 scfm (240 acfm) would be required. The estimated December 1979 installation cost for the system is $500,000. The cost and VOC reduction data for this vent are shown in Table D-4.

C. STRIPPER PURGE VENT——OXYGEN-OXIDATION PROCESS

For the model plant it was calculated that a 20-hp compressor handling 53 scfm (12 acfm) would be required; the size of this compressor can be very site specific, depending on the plant operating conditions. One producer calculates that this compressor would be 200 hp for their conditions.[3] The estimated December 1979 installation cost for the system is $55,000. The control cost data are shown in Table D-5.

Table D-2. Catalytic Oxidizer Control Cost Data for Air-Oxidation Process

Plant Size (Gg)	Waste-Gas Rate (scfm)	Installed Capital Cost[a]	Annual Cost (X 1000)							VOC Reduction (Mg/yr)	Cost Effectiveness (per Mg)
			Fixed[b]	Catalyst[c]	Fuel[d]	Power	Man-power[e]	Credit[f]	Net		
			No Heat Recovery								
100	29,000	$ 780	$ 226	$ 41	$ 478	$ 37	$18		$ 800	$ 5,660	$141
227	65,000	1,500	435	86	1086	85	18		1710	12,850	133
500	143,000	2,900[g]	841	176	2392	186	18		3613	28,300	128
			With 100-psig Steam Waste Heat Generator								
100	29,000	1,400	406	41	478	37	36	$ (647)	351	5,660	62
227	65,000	2,600	754	86	1,086	85	36	(1468)	579	12,850	45
500	143,000	4,800[b]	1,392	176	2,392	186	36	(3233)	949	2,830	34

[a] Interpolated from Fig. IV-2. of ref 1.

[b] From Table VI-5 of this report, 29% of installed capital.

[c] From Table II-1 of ref 1. Flue gas to waste gas ratio is 1.58; this value times the waste-gas rate gives the flue-gas rate. Then interpolating from Fig. A-2, the purchase cost of catalyst is obtained. Adding a 20% installation cost and dividing by a 3-yr catalyst life (example, p. B-3) gives the annual catalyst cost.

[d] From Table II-1 of ref 1 15.9 Btu/scf is required at \$2.00/thousand ft^3 (Table VI-5 of this report); this yields the annual cost.

[e] Calculated as in examples on p. B-3 of ref 1.

[f] From Fig. II-2 of ref 1. Flue-gas heat content at 1150°F is 22 Btu/scf and at 500°F exit boiler temperature the heat recovery is 62%, or 13.6 Btu/scf of flue gas or 13.6 X 1.58 = 21.5 Btu/scf of waste gas. Then from the waste-gas flow and the value of steam from Table VI-5 the credit is calculated.

[g] Assumed to be two half-size units at 85% of individual unit cost.

Table D-3. Thermal Oxidizer Control Cost Data for Air-Oxidation Process

Plant Size (Gg)	Waste Gas Rate (scfm)	Installed Capital Cost[a]	Annual Cost[a] (X 1000)					VOC Reduction (mg/yr)	Cost Effectiveness (per Mg)
			Fixed	Utilities	Manpower	Recovery Credit	Net		
					No Heat Recovery				
100	29,000	$1100	$319	$1899	$18		$ 2,236	5,900	$379
227	65,000	1400	406	4310	18		4,734	13,390	354
500	143,000	2550	740	9493	18		10,251	29,500	348
					With 250-psig Steam Waste Heat Generator				
100	29,000	$1800	$ 522	$1899	$36	$(1556)	$ 901	5,900	$153
227	65,000	3100	899	4310	36	(3532)	1,713	13,390	128
500	143,000	5780	1676	9493	36	(7779)	3,426	29,500	116

[a] Values are interpolated from data given on p B-19 of the Thermal Oxidation report (ref 2).

Table D-4. Stripper Purge Vent Control Cost Data for Air-Oxidation Process

Plant Size (Gg)	VOC Reduction (Mg/yr)	Installed Capital Cost	Annual Cost (X 1000)					Cost Effectiveness (per Mg)
			Fixed Cost	Utilities	Manpower	Recovery Credit	Net	
100	385	$305	$ 88	$ 22	$5	$ (52)[a]	$63	$164
227	875	500	145	49	5	(118)[a]	81	93
500	1925	800	232	108	5	(260)[a]	85	44

[a] Savings.

Table D-5. Stripper Purge Vent Control Cost Data for Oxygen-Oxidation Process

Plant Size (Gg)	VOC Reduction (Mg/yr)	Installed Capital Cost	Annual Cost (X 1000)					Cost Effectiveness (per Mg)
			Fixed Cost	Utilities	Manpower	Recovery Credit	Net	
40	112	$26	$ 8	$1	$4	$(16)[a]	$(31)	$(30)
136	382	55	16	4	4	(55)[a]	(31)	(81)
250	707	80	23	7	4	(101)[a]	(67)	(95)

[a] Numbers in parentheses reflect a savings.

D. REFERENCES*

1. J. A. Key, IT Enviroscience, Control Device Evaluation. Catalytic Oxidation (October 1980) (EPA/ESED report, Research Triangle, Park, NC).

2. J. W. Blackburn, IT Enviroscience, Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED, Research Triangle Park, NC).

3. J. Starkey, Northern Petroleum Co., letter dated May 2, 1979, to EPA with information on 60 processes.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX E

EXISTING PLANT CONSIDERATIONS

Table E-1 lists some emission control devices reported to be used by industry. To gather information for the preparation of this report, three site visits were made to manufacturers of EO. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Research Triangle Park, NC.[1—3] Some of the pertinent information concerning process emissions from existing EO plants is presented in this appendix. Pertinent information was also obtained from the Chemical Manufacturers Association and from some producers who submitted comments in response to the draft of this report issued in November 1978.

A. PROCESS EMISSIONS FROM EXISTING PLANTS

1. BASF Wyandotte Corporation, Geismar, LA[1]

The ethylene oxide facility consists of two trains of equipment, one constructed in 1957 but with later major revisions and the other constructed in 1967. The following are reported emissions:

a. Tail Gas Absorber——The light ends from this residual absorber are recycled to the ethylene oxide absorber. Its composition is shown below:

	Amount (vol %)	
Component	Unit 1	Unit 2
O_2	1.0	0.9
C_2H_2	26.5	21.8
CH_4	11.5	9.5
CO_2	54.2	62.5
N_2	0.4	0.5
Ar	5.8	4.8
H_2O	0.4	

Table E-1. Emission Control Devices Used by Some Domestic Ethylene Oxide Producers

Source	Control Devices Used		
	By Union Carbide Corp.[a] (Air-Oxidation)	By Celanese Chemical Co.[b] (Oxygen-Oxidation)	By BASF Wyandotte Corp.[c] (Oxygen-Oxidation)
Main process vent	Catalytic oxidation	Not applicable (NA)	NA
CO_2 purge vent	NA	Transferred to another process	None
Argon purge vent	NA	Utility boiler fuel with flare alternate	Utility boiler fuel
Stripper purge vent	Compression and recycle	Compression and recycle	Compression and recycle
Fugitive	Engineering design and operating measures	Not reported (NR)	NR
Storage and handling	Scrubbers and flare	Scrubber	Flare
Secondary	NR	Cooling tower mist eliminators	NR

[a] See ref 1.

[b] See ref 2.

[c] See ref 3.

Other characteristics are as follows:

Temperature:	unit 1, 85°F; unit 2, 85°F
Pressure:	unit 1, 48 psig; unit 2, 54 psig
Flow rate:	unit 1, 1050 lb/hr; unit 2, 800 lb/hr

This overhead stream is vented to the atmosphere for approximately 5 to 10 min three to four times a year. This conditioning is caused by a gas overload on the compressor.

b. Main Process Vent -- This vent, which is a slipstream of the recycle stream to the reactors, is piped to the utility boilers. The composition is as follows:

	Amount (vol %)	
Component	Unit 1	Unit 2
O_2	4.1	5.5
C_2H_4	23.0	23.0
CH_4	47.0	51.0
CO_2	9.0	11.0
C_2H_6	0.1	0.1
N_2	9.0	3.7
Ar	7.0	4.8
H_2O	0.9	0.9

The flow rate for unit 1 is 1800 lb/hr and for unit 2 is 650 lb/hr.

c. Carbon Dioxide Purge Vent -- This vent goes to the atmosphere. The outlets from both systems have a temperature of 215°F. The composition of this vent from the two plants is as follows:

	Weight Percent	
Component	Unit 1	Unit 2
Water	53.3	53.3
CO_2	46.5	46.5
Ethylene	0.2	0.2

The flow rate for unit 1 is 31,360 lb/hr and for unit 2 is 23,300 lb/hr. On a water-free basis the CO_2 from the stripper overhead contains approximately 0.84 mole % ethylene and 0.44 mole % methane.

2. Celanese Chemical Company, Pasadena, TX[2]

The ethylene oxide facility consists of a single train of equipment with four parallel reactors. The emissions from four process sources are given in Table E-1.

B. TOTAL INDUSTRY EMISSIONS

Emissions from industry were estimated based on the control measures reported by plants and on the assumption that similar control measures exist for the other plants. It was estimated that secondary emissions are uncontrolled for all plants and that maintenance programs required for safety reasons in EO plants result in controlled fugitive emissions.

Based on the above, total emissions from all plants during 1978 were approximately 8 Gg. The emissions from these plants would have been approximately 113 Gg if they had been uncontrolled.

C. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

Table E-2. Emission Data for Process Vents

Component	Weight Percent	Capacity (lb/1000 lb of EO) 85%	100%
		Adsorption/Desorption System Vent	
CO_2	11.7	1.36	1.39
C_2H_6	0.3	0.02	0.04
C_2H_4	29.4	2.80	3.49
CH_4	24.0	2.80	2.84
N_2	8.4	1.00	1.00
O_2	5.7	0.67	0.63
Ar	20.4	2.37	2.42
Total		11.02	11.81
		Carbon Dioxide Removal System Vent	
CO_2	99.44	628.0	678.3
C_2H_4	0.56	3.5	3.8
Total		631.5	682.1
		Vent Absorber Vent	
N_2	99.9+	443 (lb/hr)	
		Pressure Swing Adsorption Vent	
CH_4	91.2	8.52	8.84
N_2	0.6	0.05	0.06
CO_2	2.0	0.20	0.19
C_2^{--}	4.9	0.47	0.48
C_3^{--}	0.2	0.02	0.02
C_4^{--}	0.9	0.10	0.10
Total		9.36	9.69

E. REFERENCES*

1. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Union Carbide Corp., South Charleston, WV, Dec. 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. J. F. Lawson, IT Enviroscience, Trip Report for Visit to Celanese Chemical Co., Clear Lake City, TX, June 21 and 22, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. J. F. Lawson, IT Enviroscience, Trip Report for Visit to BASF Wyandotte Corp., Geismar, LA, July 11, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

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REPORT 5

VINYL ACETATE

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This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

D11I

CONTENTS OF REPORT 5

Page

I. ABBREVIATIONS AND CONVERSION FACTORS I-1

II. INDUSTRY DESCRIPTION II-1
- A. Introduction II-1
- B. Vinyl Acetate Usage and Growth II-1
- C. Domestic Producers II-1
- D. References II-4

III. PROCESS DESCRIPTION III-1
- A. Introduction III-1
- B. Ethylene Vapor-Phase Process: Bayer III-1
- C. Acetylene Process III-5
- D. References III-6

IV. EMISSIONS IV-1
- A. Typical Plant IV-1
- B. Sources and Emissions IV-1
- C. Reference IV-6

V. APPLICABLE CONTROL SYSTEMS V-1
- A. Inert-Gas Purge Vent V-1
- B. CO_2 Vent V-1
- C. Emergency Vents V-1
- D. Light-Ends and Inhibitor-Tank Vents V-3
- E. Storage and Handling Sources V-3
- F. Current Emission Controls V-3
- G. References V-4

VI. IMPACT ANALYSIS VI-1
- A. Environmental Impact VI-1
- B. References VI-4

APPENDICES OF REPORT 5

A. PHYSICAL PROPERTIES OF VINYL ACETATE, ACETALDEHYDE, METHYL ACETATE, AND ETHYL ACETATE A-1

B. EXISTING PLANT CONSIDERATIONS B-1

TABLES OF REPORT 5

Number		Page
II-1	Vinyl Acetate Usage and Growth	II-2
II-2	Vinyl Acetate Capacity	II-3
IV-1	Emissions from Uncontrolled Typical Plant	IV-2
IV-2	Typical Plant Storage	IV-4
V-1	Emissions from Controlled Typical Plant	V-2
VI-1	Environmental Impact of Control	VI-2
VI-2	Emission Ratios for Typical Plant and Industry	VI-3
A-1	Physical Properties of Vinyl Acetate	A-1
A-2	Physical Properties of Acetaldehyde	A-2
A-3	Physical Properties of Methyl Acetate	A-3
A-4	Physical Properties of Ethyl Acetate	A-4
B-1	Emission Control Devices Currently Used	B-2
B-2	Direct Emissions (Union Carbide)	B-3
B-3	Secondary Emissions (Union Carbide)	B-3
B-4	Direct Emissions (Celanese	B-5
B-5	Secondary Emissions (Celanese)	B-5
B-6	Direct Emissions (Du Pont)	B-6

FIGURES OF REPORT 5

Number		Page
III-1	Process Flow Diagram	III-3

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

Vinyl acetate production was selected for study because preliminary estimates indicated total emissions of volatile organic compounds (VOC) from the industry were relatively high and because an increase in consumption was expected to continue.

Vinyl acetate is a flammable liquid boiling at 72.2°C. It tends to polymerize and must be suitably inhibited during storage and handling. Appendix A gives the pertinent physical properties of vinyl acetate.

B. VINYL ACETATE USAGE AND GROWTH

The production of vinyl acetate in the United States for 1976 was 656 Gg. Vinyl acetate consumption is expected to increase at an average annual rate of 5 to 7.5% and to reach 880 to 1012 Gg in 1982.[1]

The uses of vinyl acetate and their expected growth rates are given in Table II-1. The major end uses are in the paint and the paper manufacturing industries. Twenty three percent of production is exported.[1]

C. DOMESTIC PRODUCERS

Currently vinyl acetate is being produced at seven manufacturing sites. Some capacity data for these sites were obtained from the literature,[1] some from site visits,[2],[3] and some from responses to EPA requests for information.[4-6] Table II-2 lists the current producers, their plant locations, their capacities, and the processes employed. Vinyl acetate production requires either captive or merchant supply of the hydrocarbon raw material (ethylene or acetylene); therefore a Gulf Coast location is economically favored.

With a total domestic industry capacity of 1060 Gg/yr and a demand projection of 880 to 1012 Gg/yr for 1982 it is likely that there will be some capacity added within this five-year period.[7,8] The economics of the ethylene and the acetylene processes indicates that the ethylene process will more likely be chosen for the added capacity and that it will ultimately replace the acetylene-based production.

Table II-1. Vinyl Acetate Usage and Growth[a]

End Use	Production for 1976 (%)	Average Growth for 1976--1982[b] (%/yr)
Polyvinyl acetate emulsions and resins	47	5--7
Polyvinyl alcohol	17	7--9
Polyvinyl butyral	5	3--5
Vinyl chloride copolymers	4	3--5
Ethylene/vinyl acetate resins	4	12--15
Other uses	1	3--5
Exports	23	5--7
Average		5--7.5[c]

[a] See ref. 1.

[b] Projection from 1981--1982 is estimated to be at same rate as from 1976--1981.

[c] Weighted arithmetic average.

Table II-2. Vinyl Acetate Capacity

Producer	Location	Capacity (Gg/yr)	Process
Borden Inc.	Geismar, LA	68[a]	Acetylene
Celanese Chemical Co.	Bay City, TX	180+[b]	Ethylene, vapor phase
	Clear Lake, TX	180[a]	Ethylene, vapor phase
E. I. du Pont de Nemours and Co.	LaPorte, TX	180[c]	Ethylene, vapor phase
National Distillers and Chemical Corporation U. S. Industrial Chemicals Co. Division	Deer Park, TX	270[d]	Ethylene, vapor phase
National Starch and Chemical Corp.	Long Mott, TX	23[e]	Acetylene
Union Carbide Corp.	Texas City, TX	159[f]	Ethylene, vapor phase
Total		1060	

[a] See ref. 1.

[b] See ref. 2.

[c] See ref. 4.

[d] See ref. 5.

[e] See ref. 6.

[f] See ref. 3.

D. REFERENCES*

1. H. E. Frey et al., "CEH Marketing Research Report on Vinyl Acetate, Polyvinyl Alcohol," pp. 580.1871A--580.1872Z in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, GA (September 1977).

2. S. W. Dylewski, Hydroscience, Inc., Trip Report for Visit to Celanese Chemical Company, Bay City, TX, Sept. 28 and 29, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. S. W. Dylewski, Hydroscience, Inc., Trip Report on Information Obtained on Vinyl Acetate Process Used at Union Carbide Corporation, Texas City, TX Plant, Dec. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. D. W. Smith, letter to EPA from E.I. du Pont de Nemours and Company, Inc., La Porte, TX, Sept. 18, 1978, in response to EPA's request for information on the vinyl acetate process.

5. K. G. Carpenter, letter from U.S. Industrial Chemicals Company, Deer Park, TX, Aug. 17, 1978, in response to EPA's request for information on the vinyl acetate process.

6. E. W. Bousquet, letter from National Starch and Chemical Corporation, Long Mott, TX, Aug. 22, 1978, in response to EPA's request for information on the vinyl acetate process.

7. "Chemical Profile on Vinyl Acetate," p. 9 in Chemical Marketing Reporter, Oct. 6, 1975.

8. "Chemical Profile on Vinyl Acetate," p. 9 in Chemical Marketing Reporter, Oct. 9, 1978.

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*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

In the United States two processes are currently in use for the manufacture of vinyl acetate. The ethylene--acetic acid--oxygen vapor-phase (ethylene vapor-phase) process accounts for about 92% of the production (see Table II-2). The acetylene--acetic acid vapor-phase (acetylene) process accounts for the balance of the production. This has changed markedly from 1970, when the acetylene process accounted for most of the world's production.[1]

Both Bayer AG (Bayer) and U.S. Industrial Chemicals (U.S.I.) developed ethylene vapor-phase processes separately and have offered to license to others. The ethylene-based processes are favored over the acetylene process because ethylene is a lower cost raw material.[2]

Other processes have been used, such as the liquid process based on ethylene. Still other processes show promise for the future, such as the one that uses only ethylene and oxygen as raw materials.[2]

B. ETHYLENE VAPOR-PHASE PROCESS: BAYER

1. Chemistry

Ethylene reacts with acetic acid and oxygen in the presence of palladium catalysts[1] to form vinyl acetate as shown in reaction 1. About 90% of the ethylene reacts in this fashion. About 10% of the ethylene is oxidized to CO_2 according to reaction 2. Less than 1% of the ethylene is oxidized to other species such as acetaldehyde, ethylacetate, and methyl acetate, of which acetaldehyde is predominant (see reaction 3).

Reaction 1:

$$\underset{\text{(ethylene)}}{H_2C{=}CH_2} + \underset{\text{(acetic acid)}}{CH_3COOH} + \underset{\text{(oxygen)}}{1/2O_2} \longrightarrow \underset{\text{(vinyl acetate)}}{CH_3COOCH{=}CH_2} + \underset{\text{(water)}}{H_2O}$$

Reaction 2:

$$\underset{\text{(ethylene)}}{H_2C{=}CH_2} + \underset{\text{(oxygen)}}{3O_2} \longrightarrow \underset{\text{(carbon dioxide)}}{2CO_2} + \underset{\text{(water)}}{2H_2O}$$

Reaction 3:

$$\underset{\text{(ethylene)}}{H_2C{=}CH_2} + \underset{\text{(oxygen)}}{1/2O_2} \longrightarrow \underset{\text{(acetaldehyde)}}{CH_3CHO}$$

2. Process Description

The process flow diagram shown in Fig. III-1 represents a typical continuous ethylene vapor-phase process under the Bayer license.[1--4] Recycled and fresh acetic acid (Stream 1) and recycled and fresh ethylene (Stream 2) are fed to a vaporizer.

The heated gaseous mixture is combined with oxygen to form the desired reaction mixture (Stream 3). The organic content of the mixture is controlled at about 85% and the oxygen content is controlled at about 7% to keep the gas composition outside the explosive range. Other components of the gas stream are CO_2, H_2O, and inert gases.[2]

The gaseous reaction mixture (Stream 3) is fed to the reactor containing a fixed-bed suspended catalyst that includes palladium, gold, and salts of potassium. Because of the low oxygen and high ethylene content of the reaction mixture, only about 10% of the ethylene is converted per pass.[2]

The reactor discharge (Stream 4) is first passed through an energy recovery step to make use of the heat liberated in the reaction and then to the first gas-liquid separator.

The gas, mainly ethylene laden with acetic acid and vinyl acetate vapors (Stream 5), is scrubbed with acetic acid to absorb the condensable materials and to combine them with the reactor liquid stream.

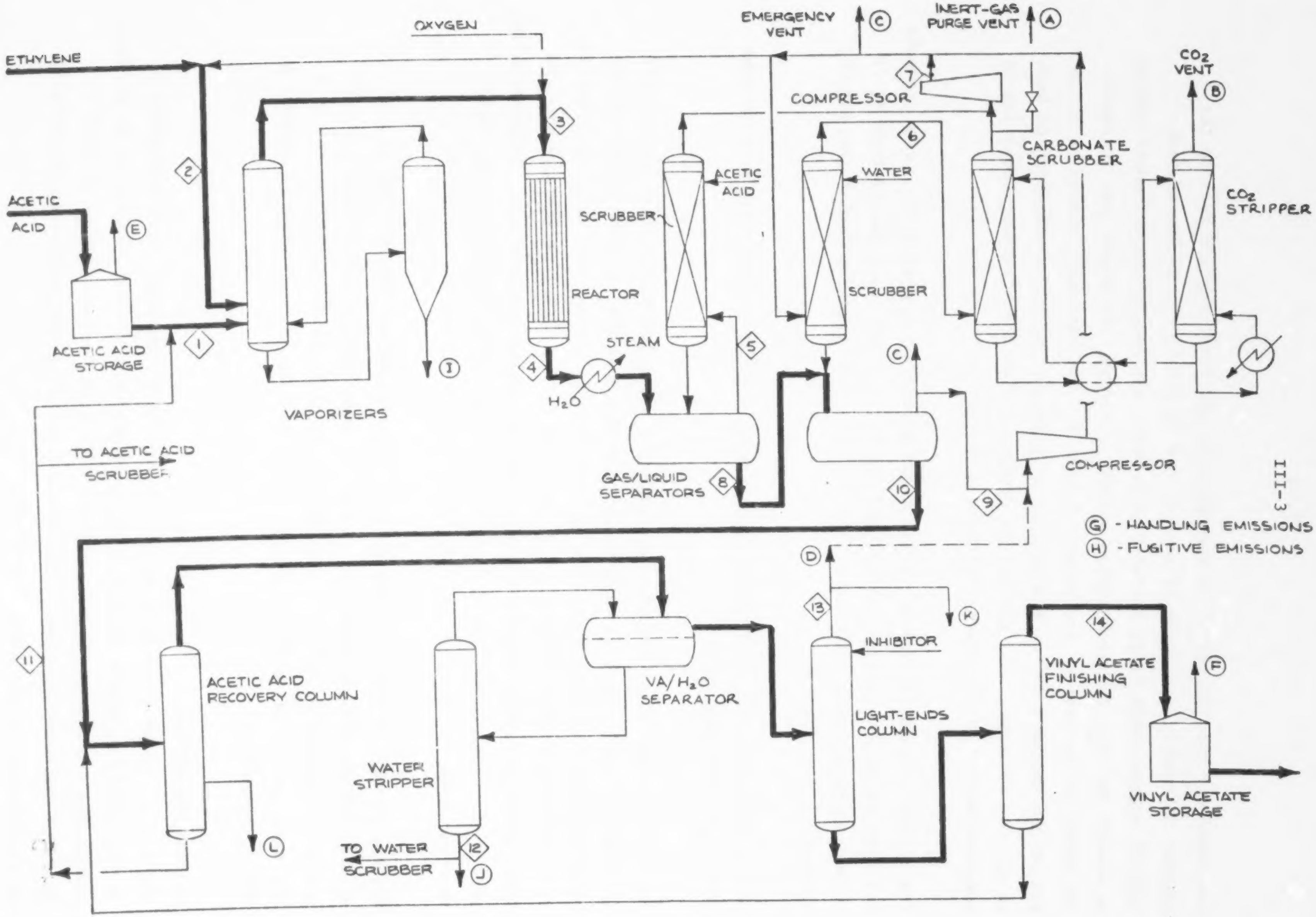

Fig. III-1. Flow Diagram for Manufacture of Vinyl Acetate by the Ethylene Vapor-Phase Process

The resultant gas (Stream 6) is recompressed and then recycled back to the reactor (Stream 7). A purge of recycle gas is fed to the carbon dioxide removal system where it is scrubbed with water and fed to the carbonate system to absorb the CO_2. The inert gases ethane, nitrogen, and argon that accompany the feeds to the reactor are purged at vent A. The carbonate stream is stripped of the absorbed CO_2 by the release of pressure and the application of heat in the CO_2 stripper. The gas stream resulting from the stripping operation is composed mainly of CO_2 and is discharged at vent B.

The reactor liquid (Stream 8), still under pressure, is passed through a pressure let-down valve and a second gas-liquid separator. The flash gas (Stream 9) is recompressed and then returned to the reactor; the remaining liquid (Stream 10) is sent to distillation.

During emergency and planned shutdowns pressure-relief valves will release some VOC at the vent marked C.

The distillation steps recover, in sequence, unreacted acetic acid for recycle (Stream 11), water that is made in the reaction and that is used in gas scrubbing (Stream 12), light ends such as acetaldyhyde (Stream 13), and vinyl acetate as a finished product (Stream 14). The low-boiling nature of acetaldehyde and other light ends may result in some discharge during distillation. Polymerization inhibitors, introduced during distillation, are dissolved in mix tanks which generate some VOC emission. These emissions are discharged at vent D.

Polymer wastes, formed in reaction and in distillation, are carried in acetic acid in stream 11, and after two stages of vaporization the solids are discharged at stream I. Water formed in the reaction is discharged at stream J. The small amount of acetaldehyde and ethyl acetate is discharged at streams K and L, respectively.

3. Process Variations

The U.S.I. process is quite similar to the Bayer process. The difference is in the reaction, where the U.S.I. process produces a wider variety of by-products, and in the scrubbing steps, in which a glycol diacetate scrubber is used in place of the water scrubber. The steps for the two processes can essentially be represented by the same flow sheet.[5]

C. ACETYLENE PROCESS

Acetylene and acetic acid react readily in the presence of zinc acetate to form vinyl acetate according to the following reaction:

$$\underset{\text{(acetylene)}}{HC{\equiv}CH} \quad + \quad \underset{\text{(acetic acid)}}{CH_3COOH} \quad \xrightarrow{\text{catalyst}} \quad \underset{\text{(vinyl acetate)}}{CH_3COOCH{=}CH_2}$$

The reaction is conducted in the vapor phase, with both raw materials being present in excess. The unconverted raw materials are recovered and recycled. Ethylene, present as an impurity in the acetylene and being essentially inert, must be purged from the reaction system. This is done by discharging a portion of the unreacted acetylene. Acetaldehyde is also formed in the reaction and must be disposed of. The steps following the reaction are simpler than in the ethylene vapor-phase process because of the absence of oxidation by-products.[6]

Since the industrial use of this process is now minimal and is expected to be phased out, it will not be discussed further in this study.

D. REFERENCES*

1. D. Rhum, "Poly (vinyl acetate)," pp. 317--353 in Kirk-Othmer Encylcopedia of Chemical Technology, 2d ed., vol 21, edited by A. Stenden et al., Interscience, New York, 1970.

2. Yen-Chen Yen, Vinyl Acetate Supplement A, pp. 21--99 in Report No. 15, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (June 1972).

3. S. W. Dylewski, Hydroscience, Inc., Trip Report for Visit to Celanese Chemical Company, Bay City, TX, Sept. 28 and 29, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. S. W. Dylewski, Hydroscience, Inc., Trip Report on Information Obtained on Vinyl Acetate Process Used at Union Carbide Corporation, Texas City, TX Plant, Dec. 2, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

5. J. W. Pervier, Houdry Division Air Products and Chemicals, Inc., "Vinyl Acetate via Ethylene," pp. VAC-1--VAC-6 in Survey Reports On Atmospheric Emissions from the Petrochemical Industry, Vol IV, EPA-450/3-73-005-d (April 1974).

6. J. W. Pervier, Houdry Division Air Products and Chemicals, Inc., "Vinyl Acetate via Acetylene" pp. VI-1--VI-7 in Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol IV, EPA-450/3-73-005-d (April 1974).

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IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals are photochemically unreactive. However, many photochemically unreactive organic chemicals are of concern and may not be exempt form regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. TYPICAL PLANT

The typical plant developed for this study has a capacity of 160 Gg/yr, based on 8760 hr* of operation per year. Although not an actual operating plant, it is typical of plants recently built. The plant utilizes the ethylene vapor-phase process licensed by Bayer and best fits today's manufacturing and engineering technology for vinyl acetate production.

The quality of the raw materials used in this study is typical of production from recently built facilities. The composition of ethylene was taken as 99.9% ethylene and the balance assumed to be ethane. The composition of oxygen was taken as 99.4% O_2 and the balance assumed to be nitrogen and argon.

B. SOURCES AND EMISSIONS

Uncontrolled emissions rates from process and storage sources in vinyl acetate production are summarized in Table IV-1 and are discussed below. The discharge locations are shown in Fig. III-1. Emissions presented in this section are based on plant trips, letters, and engineering judgment based on an understanding of the process.

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*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be corresondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation in negligible.

Table IV-1. VOC Emissions from Uncontrolled Sources in Typical Vinyl Acetate Plant

Emission Source	Stream Designation (Fig. III-1)	Emissions Ratio* (g/kg)	Emissions Rate (kg/hr)
Inert-gas purge vent	A	4.39	80.18
CO_2 vent	B	0.31	5.66
Emergency vents	C	0.013	0.26
Light-ends and inhibitor mix tank vents	D	2.8	51.1
Storage			
Acetic acid	E	0.16	2.92
Vinyl acetate	F	1.95	35.61
Total		9.62	175.73

*g of emission per kg of vinyl acetate.

1. Inert-Gas Purge Vent

The major process source of VOC emissions is released at vent A. Nitrogen, argon, and ethane, which are inert in the reaction, constitute the inert gases. These gases carry along the ethylene that is present in the recycle stream. The quantity of emission from this stream is directly related to the inert-gas content of both feed gases.

2. CO_2 Vent

The CO_2 generated in the reactor by oxidation of ethylene is released at vent B and carries with it some ethylene and ethane.

3. Emergency Vents

Equipment failure, planned shutdowns, and startups contribute some VOC emissions. These releases occur at vents C.

4. Light-Ends and Inhibitor Mix Tank Discharges

The reaction also generates acetaldehydes and other low-temperature-boiling materials. The processing of these materials results in some VOC emission. The makeup of an inhibitor solution and addition to a distillation stream result in some VOC emission. These losses occur at vent D.

5. Fugitive Emissions

No data on fugitive emissions are presented in this study. Fugitive emissions for the entire synthetic organic chemical manufacturing industry (SOCMI) are covered by separate EPA documents.

6. Storage and Handling Emissions

Emissions result from the storage of acetic acid and vinyl acetate (Vents E and F). Storage tank sizes and conditions for the typical plant are given in Table IV-2. The storage emissions in Table IV-1 are based on fixed-roof tanks, half full, and a diurnal temperature variation of 11°C and on the emission equations from AP-42.[1]

VOC emissions due to handling are not presented in this sutdy but are contained in a separate EPA storage and handling document covering the entire SOCMI.[2]

Table IV-2. Storage-Tank Data for Typical Vinyl Acetate Plant

Storage Tank Designation	Contents	No. of Tanks Required	Tank Size (m^3)	Turnovers Per Year	Bulk Temperature (°C)
Bulk storage	Acetic acid	2	5150	12	37.8 *
In-process	Acetic acid	2	675	182.5	37.8
In-process	Vinyl acetate	2	940	182.5	37.8
Bulk storage	Vinyl acetate	2	7150	12	37.8

*Temperature estimated for purpose of emission calculations.

7. Secondary Emissions

Secondary VOC emissions can result from the handling and disposal of the process-waste liquid streams such as: high-temperature-boiling polymer wastes (Discharge I), wastewater (Discharge J), light-ends waste (Discharge K), and ethyl acetate purge (Discharge L). Evaluation of the potential emissions from disposing of these and other wastes from the entire SOCMI will be covered by a future EPA secondary emissions document.

C. REFERENCE*

1. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-6 to 4.3-11 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (April 1977).

2. D. G. Erikson, Hydroscience, Inc., Storage and Handling Report (on file at EPA, ESED, Research Triangle Park, NC) (October 1978).

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V. APPLICABLE CONTROL SYSTEMS

A. INERT-GAS PURGE VENT

The inert-gas purge emissions (Vent A, Table V-1) are of fuel quality and can be disposed of readily in a fire box or thermal oxidizer, which also may be employed for disposing of the emissions discussed below. With a properly designed and operated thermal oxidizer a VOC reduction of 99% or greater can be achieved. Data and documentation to support this conclusion will be presented in a future EPA report on emission control systems.

Flaring of the inert purge gas is practiced in some plants;[1,2] however, in the typical plant this stream is extremely small. Unless the flare diameter is designed for the gas rate, the efficiency may be as low as 95%.[3] (This is further discussed later in this section.)

B. CO_2 VENT

The CO_2 vent gas (Vent B) has a very low fuel value and will not self-sustain combustion; it can, however, be fed as a fume to the thermal oxidizer mentioned above and as is practiced in some plants.[2,4] With proper design and operation a VOC reduction of 99% or greater can be achieved.

The CO_2 vent gas can also be flared; however, the fuel value of all the process vent streams combined would not be sufficient for a stable flame to be maintained in a flare, and supplemental fuel would be required. With proper design and operation an emission reduction of at least 99% is expected.[3]

C. EMERGENCY VENTS

Venting during periodic unscheduled or emergency-equipment outages require the safe handling of a large quantity of VOC (Vents C). It is estimated that a flare properly designed for emergency releases and properly maintained can result in an emission reduction of 98%.[3] The gas venting rate during emergency-equipment outage will require a flare much larger than the one that would be required to control the emissions during normal operation.

Table V-1. VOC Emissions from Controlled Sources in Typical Vinyl Acetate Plant

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emissions Ratio[a] (g/kg)	Emissions Rate (kg/hr)
Inert-purge vent	A	Fire box/thermal oxidizer	99	0.044	0.80
CO_2 vent	B	Thermal oxidizer/ flare	99[b]	0.003	0.05
Emergency vents	C	Flare	98[b]	0.0005	0.009
Light-ends and inhibitor mix tank vents	D	Fire box/thermal oxidizer	99	0.028	0.51
Storage					
Acetic acid	E	None		0.26	4.75
Vinyl acetate	F	Floating roof	96	0.10	1.83

[a] g of emission per kg of vinyl acetate.

[b] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies cited are for tentative comparison purposes.

D. LIGHT-ENDS AND INHIBITOR-TANK VENTS

The light-ends and the inhibitor-tank vent gas emissions (Vents D) are of fuel quality and can be disposed of readily in a fire box or thermal oxidizer. A VOC emission reduction of 99% or greater can be achieved as discussed above.

Flaring the vent gas with proper design and operation can also result in an emission reduction of at least 99%.[3]

E. STORAGE AND HANDLING SOURCES

1. Acetic Acid Storage

Emission of acetic acid due to tank breathing and filling is small and is uncontrolled in this typical plant (Vent E).

2. Vinyl Acetate Storage

Internal floating-roof tanks* are used in the industry for emission control in vinyl acetate storage and are used in the typical plant. The controlled vinyl acetate emissions given in Table V-1 were calculated with the modified AP-42 floating-roof storage-tank emission equations.[5--7]

3. Handling

Control of emissions due to handling are not presented in this study but are included in a separate EPA storage and handling document covering the entire SOCMI.[8]

F. CURRENT EMISSION CONTROLS

Emission control devices currently used by some domestic vinyl acetate producers are shown in Appendix B.

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*Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed. (fixed-roof tanks with internal floating device to reduce vapor loss).

G. REFERENCES*

1. S. W. Dylewski, Hydroscience, Inc., Trip Report Information Obtained on Vinyl Acetate Process Used at Union Carbide Corporation, Texas City, TX, Plant, Dec. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. D. W. Smith, letter to EPA from E.I. du Pont de Nemours and Company, Inc., La Porte, TX, Sept. 18, 1978, in response to EPA's request for information on the vinyl acetate process.

3. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, N.C.

4. S. W. Dylewski, Hydroscience, Inc., Trip Report for Visit to Celanese Chemical Company, Bay City, TX, Sept. 28 and 29, 1977 (on file at EPA, ESED, Research Triangle Park, NC)

5. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-6 to 4.3-11 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (April 1977).

6. Chicago Bridge and Iron, SOHIO/CBI Floating Roof Emission Testing Program, Supplemental Report (Feb. 15, 1977).

7. Equation for floating-roof withdrawal loss derived by R. Burr, EPA, ESED, Research Triangle Park, NC.

8. D. G. Erikson, Hydroscience, Inc., Storage and Handling Report (on file at EPA, ESED, Research Triangle Park, NC) (October 1978).

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VI. IMPACT ANALYSIS

A. ENVIRONMENTAL IMPACT

1. Typical Plant

The environmental impact of the application of the described control systems to the typical plant would be a VOC emission reduction of 1625 Mg/yr compared to an uncontrolled plant, as shown in Table VI-1.

2. Industry

Emission sources, control levels, and emission ratios for the typical plant are summarized in Table VI-2. From emission data reported by producing vinyl acetate plants[1--3] the emission ratios for the industry have been estimated and are also shown in Table VI-2. These values show that the industry processes as represented by the Bayer process are about 96% controlled. With a 1978 production level of 740 Gg and the assumption that the emissions from the industry are at the same ratio as for the Bayer process, the emissions from industry are estimated to be 247 Mg.*

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*Fugitive, secondary, storage, and handling emissions are not included.

Table VI-1. Environmental Impact of Controlled Sources in a Typical Vinyl Acetate Plant*

Source	Stream Designation (Fig. III-2)	Control Device or Technique	Total VOC Emission Reduction (%)	Total VOC Emission Reduction (Mg/yr)
Inert-gas purge vent	A	Fire box/thermal oxidizer	99	695.4
CO_2 vent	B	Thermal oxidizer/ flare	99	49.1
Emergency vents	C	Flare	98	4.0
Light-ends and inhibitor mix tank vents	D	Fire box/thermal oxidizer	99	443.0
Storage				
Acetic acid	E	None		
Vinyl acetate	F	Internal floating-roof tank	96	433.5
Total				1625

*Fugitive, secondary, and handling emissions are not included.

Table VI-2. Emission Ratios for Typical Plant and for Industry for Bayer Process

	Emission Ratio (g/kg)[a]		
	Typical Plant		
Emission Source	Uncontrolled	Controlled	Industry[b]
Inert-gas purge vent	4.39	0.044	0.079
CO_2 vent	0.31	0.003	0.153
Emergency vent	0.025	0.0005	0.001
Light ends } Tank vents	2.8	0.028	0.030
Inhibitor Mix } Tank vents			0.071
Total direct emissions	7.525	0.0755	0.334
Reduction		99%	95.6%

[a] g of emission per kg of vinyl acetate.

[b] Average data; see refs. 1--3.

B. REFERENCES*

1. S. W. Dylewski, Hydroscience, Inc., Trip Report for Visit to Celanese Chemical Company, Bay City, TX, Sept. 28 and 29, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. S. W. Dylewski, Hydroscience, Inc., Trip Report for Visit to Union Carbide Corporation, Texas City, TX Plant, Dec. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. D. W. Smith, letter to EPA from E.I. du Pont de Nemours & Company, Inc., La Porte, TX, Sept. 18, 1978, in response to EPA's request for information on the vinyl acetate process.

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APPENDIX A

Table A-1. Physical Properties of Vinyl Acetate*

Synonyms	Acetic acid, vinyl ester, acetic acid, ethenyl ester
Molecular formula	$C_4H_6O_2$
Molecular weight	86.09
Physical state	Liquid (polymerizes)
Vapor pressure	107.5 mm of Hg at 25°C
Vapor specific gravity	3.0
Boiling point	72.2 to 72.3°C at 760 mm of Hg
Melting point	-93.2°C
Density	0.9317 at 20°C/4°C
Water solubility	Insoluble; soluble in hot H_2O

*From: J. Dorigan *et al.*, "Vinyl Acetate," p. AIV-286 in Appendix IV, Rev. 1 (Chemicals O--Z), to *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals*, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properties of Acetaldehyde*

Synonyms	Acetic aldehyde, Ethyl aldehyde
Molecular formula	C_2H_4O
Molecular weight	44.05
Physical state	Liquid
Vapor pressure	923 torrs at 25°C
Vapor specific gravity	1.52
Boiling point	20.8°C at 760 mm
Melting point	-121°C
Density	0.7834 at 18°C/4°C
Water solubility	Infinite (hot)

[*] From: J. Dorigan *et al*, "Acetaldehyde" p. AI-6 in Appendix I, Rev. 1, (Chemicals A-C), to *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals*, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-3. Physical Properties of Methyl Acetate*

Synonyms	Acetic acid, methyl ester
Molecular formula	$C_3H_6O_2$
Molecular weight	74.08
Physical state	Liquid
Vapor pressure	212.5 mm at 25°C
Vapor specific gravity	2.55
Boiling point	57.8°C
Melting point	-98.1°C
Density	0.9330 at 20°C/4°C
Water solubility	Very soluble

*From: J. Dorigan et al, "Methyl Acetate" p. AIII-148 in Appendix III, Rev. I, (Chemicals F-N), to Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-4. Physical Properties of Ethyl Acetate*

Synonyms	Acetic ester, ethyl etharate
Molecular formula	$C_4H_8O_2$
Molecular weight	88.10
Physical state	Liquid
Vapor pressure	92.5 mm at 25°C
Vapor specific gravity	3.04
Boiling point	77.06°C at 760 mm
Melting point	-83.58°C
Density	0.8946 at 25°C/4°C
Water solubility	Soluble (89 gm/liter)

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[*] From: J. Dorigan _et al_, "Ethyl Acetate" p. AII-234 in Appendix II, Rev. 1, (Chemicals D-E), to _Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals_, MTR-7248, MITRE Corp., McLean, VA (September 1976).

APPENDIX B

EXISTING PLANT CONSIDERATIONS

Table B-1 lists process control devices reported to be in use by industry. To gather information for the prepation of this report site visits were made to manufacturers of vinyl acetate. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Research Triangle Park, N.C.[1,2]

A. PROCESS EMISSIONS FROM EXISTING PLANTS

1. Union Carbide Corp., Texas City, Texas[1]

Union Carbide Corp. at Texas City, Texas manufactures vinyl acelate (VA) by oxidation of ehtylene and acetic acid. The plant, of single train design, was started in 1975 and has a capacity of 350 MM lb/yr. Acetic acid is received by barge; ethylene and oxygen are supplied by other facilities at the Texas City site. The product is shipped by marine tankers and barges.

Barger AG and U.S. Industrial Chemicals both have patents on the vapor pahse oxidation of a mixture of ethylene and acetic acid. The direct VOC emissions reported before and after the emission control device (ECD) are shown by Table B-2. There are several liquid streams that are removed from the process where secondary emissions may be experienced. These streams are tabulated in Table B-3.

2. Celanese Chemical Co., Bay City, Texas[2]

The Celanese Chemical Company at Bay City, Texas, manufactures vinyl acetate (VA) by oxidation of ethylene and acetic acid. Acetaldehyde and acetic acid are also manufactured in separate plants at this site. The capacity is stated to be 400 MM lb/hr. The VA unit is connected to the acetaldehyde and acetic-acid units by raw material flow piping, liquid purge, and gas purge streams which aid in reducing emissions but make it difficult to segregate the emissions specific for the VA unit. Acetic acid is supplied by barge shipments in addition to the on-site manufacturing facilities. Ethylene is received by pipeline from Monsanto and Phillips Petroleum facilities located nearby. VA product is shipped mostly by barge and a minor amount by tank car and tank truck.

Table B-1. Emission Control Devices Currently Used by Some Domestic Vinyl Acetate Producers by the Bayer Process

Source	Control Devices Used by		
	Celanese Chemical Corp.[a] Bay City, TX	Union Carbide Corp.[b] Texas City, TX	Dupont[c] LaPorte, TX
Inert-gas purge vent	To another process[d]	Flare	Flare
CO_2 purge vent	Thermal oxidizer	Catalytic combustion	Thermal oxidizer
Emergency vents	Flare	Flare	No data
Light-ends vent	To another process	Flare	To atmosphere
Mix-tank vent	To atmosphere	No data	No data

[a] See ref. 2.

[b] See ref. 1.

[c] See ref. 3.

[d] Part of feed to another process; ultimately vented to a flare.

Table B-2. Direct Emissions (Union Carbide)

		lb VOC/1000 lb Product	
Source	**Polutant**	**Before ECD**	**After ECD**
CO_2 purge	Ethylene, ethane	2.63	0.067
Inerts purge*	Ethylene, ethane VA, acetaldehyde	13.0	Zero

*Emergency relief, vent header, reactor start-up, VA column vents, CO_2 purge, emergency vent.

Table B-3. Secondary Emissions (Union Carbide)

Description	Discharged to	Pollutant	Steam Rate lb/1000 lb Product
Waste polymer	Incinerator	Acetic acid, ethylidene diacetate polymers, light metal acetates	25.0
Blowdown tower (from inerts purge), flare seal pot, reactor condensate blowndown, reactor product water purge, polymer incinerator scrubber tails.	Wastewater	Vinyl Acetate	0.104
		Acetic acid and acetaldehyde	0.459
By-product residue	Boiler fuel	Vinyl acetate, acetaldehyde	10.64
Samples	Drummed (off site disposal)	Acetic acid, vinyl acetate	0.009

Barger AG and U.S. Industrial Chemicals both have patents on the vapor phase oxidation of a mixture of ethylene and acetic acid. The direct emissions reported before and after the emission control device (ECD) are shown on Table B-4. There are several points where liquids are removed from the process where emissions may be experienced as a secondary emission. These are indicated by Table B-5.

3. Du Pont, Inc., La Port, Texas[3]

The nominal capacity of the Du Pont vinyl acetate plant at La Porte, Texas is 1.1 MM lb/day. The direct emissions are reported as indicated by Table B-6. Secondary emissions may occur from the following reported waste streams:

A combination of liquid organic purges from the process. These streams average about 212 pounds per hour and are 98 wt % organic. These streams are combined with several others from two processes and incinerated in a natural gas fired incinerator.

Purge of reaction water from the process. The stream is 31 gals per minute and is combined with a flow from another process and fed to a waste disposal well system. The stream is ~0.03 wt % organic.

Purge of high boilers to the gas fixed incineration. The flow is approximately 1270 lb/hr and essentially all organic.

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

Table B-4. Direct Emissions (Celanese)

Source	Pollutant	lb VOC/1000 lb Product	
		Before ECD	After ECD
Emergency vent from reactor	Ethylene, HOAC, VA	0.0125	Zero
Inhibitor mix tank	Vinyl acetate	0.096	No ECD
Shutdown	Ethylene, HOAC, VA	0.037	Zero

Table B-5. Secondary Emissions (Celanese)

Description	Discharged to	Pollutant	Steam Rate
Vinyl acetate heavy ends	Incinerator	Confidential	Confidential
Azeotrope column side stream, water stripper, reactor inerts purge	Another process	Confidential	Confidential
Water stripper residue carbonate system blowdown	Deep well	Mostly water	Confidential
Samples	Deep well	VOC	4600 lb/yr
Sample flush	Deep well	VOC	18,300 lb/yr

Table B-6. Direct Emissions (Du Pont)

Source	Composition (wt %)	Flow
Inert gas purge vent	45% ethylene	1100 lb/hr
	10% vinyl acetate	
	2.5% acetic acid	
	40% inerts	
	2.5% misc. VOC	
CO_2 purge vent	0.3% ethylene	600 lb/hr
	99.7% CO_2	

C. REFERENCES

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*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 6

ACETALDEHYDE

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Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

October 1980

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CONTENTS OF REPORT 6

Page

I. ABBREVIATIONS AND CONVERSION FACTORS I-1

II. INDUSTRY DESCRIPTION II-1

- A. Reason for Selection II-1
- B. Acetaldehyde Usage and Growth II-1
- C. Domestic Producers II-3
- D. References II-7

III. PROCESS DESCRIPTION III-1

- A. Introduction III-1
- B. Acetaldehyde from Ethylene III-1
- C. Acetaldehyde from Ethanol III-8
- D. Acetaldehyde from Acetylene III-8
- E. Acetaldehyde from Saturated Hydrocarbons III-9
- F. Acetaldehyde from Synthesis Gas III-9
- G. References III-10

IV. EMISSIONS IV-1

- A. Acetaldehyde from Ethylene by the Two-Step Air-Oxidation Process IV-1
- B. Acetaldehyde from Ethylene by the Single-Step Oxygen-Oxidation Process IV-5
- C. References IV-7

V. APPLICABLE CONTROL SYSTEMS V-1

- A. Acetaldehyde from Ethylene by the Two-Step Air-Oxidation Process V-1
- B. Acetaldehyde from Ethylene by the Single-Step Oxygen-Oxidation Process V-4
- C. Control Measures Currently Used V-4
- D. References V-5

APPENDICES OF REPORT 6

A. PHYSICAL PROPERTIES OF ACETALDEHYDE, METHYL CHLORIDE, ETHYL CHLORIDE, AND CHLOROFORM A-1

B. FUGITIVE EMISSION FACTORS B-1

C. EXISTING PLANT CONSIDERATIONS C-1

TABLES OF REPORT 6

Number		Page
II-1	End Usage of Acetaldehyde	II-2
II-2	Acetaldehyde Capacity	II-4
IV-1	Uncontrolled Emissions for Two-Step Air-Oxidation Process	IV-2
IV-2	Composition of Uncontrolled Emissions from Two-Step Air-Oxidation Process	IV-4
V-1	Controlled Emissions for Two-Step Air-Oxidation Process	V-2
A-1	Properties of Acetaldehyde, Methyl Chloride, Ethyl Chloride, and Chloroform	A-1
C-1	Control Methods Currently Used by the Domestic Acetaldehyde Industry	C-2
C-2	High- and Low-Pressure Scrubber Emissions from Celanese Plant	C-3
C-3	High- and Low-Pressure Scrubber Emissions from Texas Eastman Plant	C-5
C-4	Estimated 1979 Acetaldehyde Industry Emissions	C-6

FIGURES OF REPORT 6

Number		Page
II-1	Locations of Plants Manufacturing Acetaldehyde	II-5
III-1	Flow Diagram for Two-Step Air-Oxidation Process	III-3
III-2	Flow Diagram for Single-Step Oxygen-Oxidation Process	III-6

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^9	1 Gg = 1 X 10^9 grams
M	mega	10^6	1 Mg = 1 X 10^6 grams
k	kilo	10^3	1 km = 1 X 10^3 meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Acetaldehyde production was selected for study because preliminary estimates indicated that the production process causes significant emissions of volatile organic compounds (VOC).

Acetaldehyde is a colorless, mobile liquid having a pungent suffocating odor that is somewhat fruity and pleasant in dilute concentrations. Some physical properties of acetaldehyde are given in Appendix A.

B. ACETALDEHYDE USAGE AND GROWTH

The current production capacity of acetaldehyde in the United States is 621 Gg/yr,[1] with the 1976 production of the order of 440 Gg or 71% of this capacity.[2] Acetaldehyde is a chemical intermediate used in the manufacture of the products shown in Table II-1.[3—7] From 90 to 95% of the acetaldehyde produced is used captively by the producer.[3]

Peak production of acetaldehyde occurred in 1969, when 749 Gg was produced. From 1969 to 1975 production declined to a low of 408 Gg/yr. The decline was largely due to phase-out of n-butanol and 2-ethylhexanol produced from acetaldehyde. These chemicals are presently made from propylene by the OXO process.[4]

Early in 1976 it was estimated that the 1976 acetaldehyde production would reach 612 Gg/yr and that production would continue to grow to 703 Gg/yr by the year 1980.[7] This would indicate an average annual growth of 3.5%. However, 1978 statistics indicate that actual 1976 production was between 431 and 445 Gg/yr and that projected production rates were not obtained.[2]

The price of acetaldehyde during the period 1950 to 1973 ranged from $0.20/kg to $0.22/kg. Since 1973, due largely to the increased cost of hydrocarbon cracking feedstocks for production of ethylene, the basic raw material used in the production of acetaldehyde, the price of acetaldehyde has increased an average of 15% per year to the current price of $0.44/kg.[8] In 1976 acetic acid production consumed 60% of the acetaldehyde produced. With the increasing cost of

Table II-1. End Usage of Acetaldehyde[a]

End Use	Acetaldehyde Consumption for 1976 (%)
Acetic acid[b]	60
Synthetic pyridine derivatives	40
Peracetic acid	
Acetate esters[c]	
Pentaerythritol	
Other uses[d]	

[a] See refs 3—7.

[b] Acetic acid is used principally for manufacture of vinyl acetate, cellulose acetate, terephthalic acid, acetic anhydride, acetate esters, chloroacetic acids, and dyestuffs.

[c] By the Tischenko process.

[d] Includes crotonaldehyde, chloral, 1,3-butylene glycol, lactic acid, and glyoxal.

ethylene feedstock, methanol carbonylation has become the preferred process for manufacture of acetic acid. Thus no growth in acetaldehyde consumption for manufacture of acetic acid is expected.[5]

The manufacture of pentaerythritol, peracetic acid, and synthetic pyridine derivatives and the manufacture of acetate esters by the Tischenko process account for the remaining 40% of the acetaldehyde consumed. This group may show strong growth in some products (pentaerythritol, used to manufacture synthetic lubricants), but even some of them may be produced by alternate processes (pyridine). The combined growth of the products in this group in not expected to take up the slack of lost acetic acid growth.[7]

The future of acetaldehyde growth appears to depend on the development of a lower cost process based on synthesis gas and an increase in demand for products produced by processes based on acetaldehyde.[5]

C. DOMESTIC PRODUCERS*

There are currently five plants producing acetaldehyde in the United States.[1,9] Table II-2 lists the producers, locations, capacities, and raw materials; Fig. II-1 shows the plant locations.

Commercial processes for the production of acetaldehyde include: the direct oxidation of ethylene, the oxidation or dehydrogenation of ethanol, the addition of water to acetylene, and the partial oxidation of hydrocarbons.[5] Acetaldehyde was first commercially produced in 1917 by hydration of acetylene.[3] As the demand increased, ethanol-based processes became the principal method used. In the 1960s, the Hoechst-Wacker process for direct oxidation of ethylene was commercialized and by 1968 became the principal method of acetaldehyde production in the United States. In 1967 there were 18 domestic plants, with a combined capacity of 754 Gg/yr. In that year 43% of the acetaldehyde capacity was based on ethylene, 31% on ethanol, 25% on propane-butane, and 1% on acetylene and

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*Since this report was first prepared (January 1979) Celanese has reportedly[10] increased its capacity from 363 Gg/yr to 431 Gg/yr. Also, it has been reported[10] that domestic consumption of acetaldehyde is expected to decline at a rate of approximately 3%/yr during the 1978—1983 period.

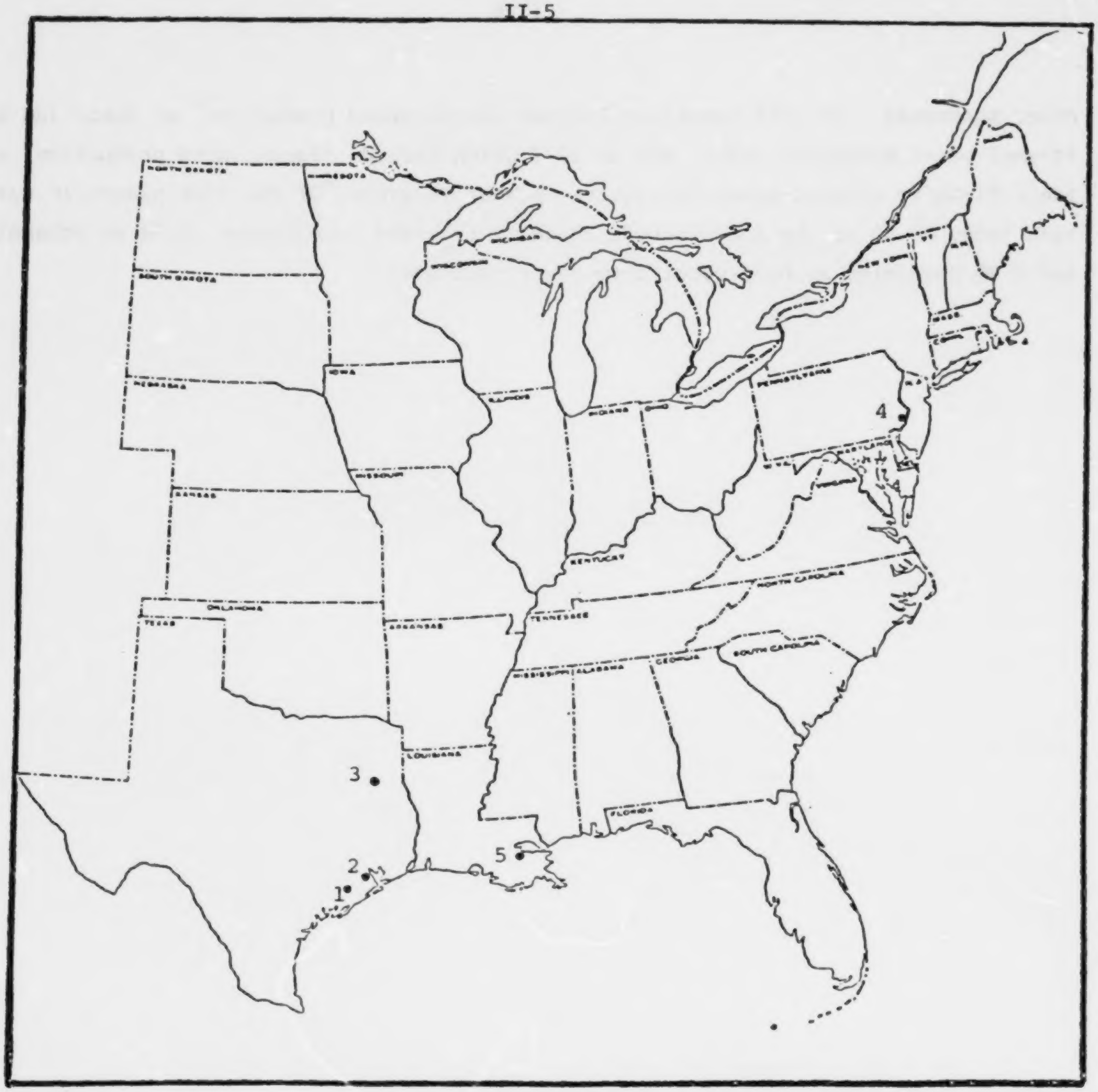
Table II-2. Acetaldehyde Capacity[a]

Company	Location	1978 Production Capacity (Gg/yr)	Basic Raw Material
Celanese Chemical Co.	Bay City, TX	136	Ethylene
Celanese Chemical Co.	Clear Lake City, TX	227[b]	Ethylene
Texas Eastman Co.	Longview, TX	227	Ethylene
Publicker Industries, Inc.	Philadelphia, PA	29[c]	Ethanol
Shell Chemical Co.	Norco, LA	2	By-product
Total		621	

[a] See ref 2.

[b] See ref 10.

[c] Publicker Industries, Inc., isolates an estimated 2.3 Gg/yr as acetaldehyde; the balance runs from ethanol through acetaldehyde (not isolated) to acetic acid.



(1) Celanese Corp., Bay City, TX
(2) Celanese Corp., Clear Lake City, TX
(3) Texas Eastman Co., Longview, TX
(4) Publicker Industries Inc., Philadelphia, PA
(5) Shell Chemical Co., Norco, LA

Fig. II-1. Locations of Plants Manufacturing Acetaldehyde

other processes. In 1966 Tennessee Eastman discontinued production[4] at their 123-Gg/yr ethanol-based Kingsport plant, and in 1977 Union Carbide discontinued production[5] at their 91-Gg/yr ethanol-based facilities in West Virginia.[4] Of the five plants in operation today 94.9% of the acetaldehyde capacity is based on ethylene, 4.7% on ethanol, and 0.4% recovered as by-product from other processes.[1]

D. REFERENCES*

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10. A. K. Rafie and S. L. Soder, "Acetaldehyde--Product Review," pp 601.5020A--601.5020M in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (March 1979).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

In the United States 94.9% of the acetaldehyde capacity is based on the Hoechst-Wacker process, which consists of two-step air oxidation of ethylene.[1] Approximately 4.7% is based on oxidation of ethanol, and the remaining 0.4% is recovered as by-product from other processes.[1] Hydration of acetylene and oxidation of saturated hydrocarbons (butane and propane), once processes of major importance in the United States, have given way to the more economic ethylene-based process. A rhodium catalyzed process capable of converting synthesis gas directly into acetaldehyde in a single step was reported in 1974.[2] This process may become important in the future as coal gasification methods are perfected.

B. ACETALDEHYDE FROM ETHYLENE

The direct liquid-phase oxidation of ethylene to acetaldehyde by means of a palladium chloride-cupric chloride catalyst was discovered in 1956.[3] The commercial process was developed and licensed by the consortium of Hoechst and Wacker in Germany in the late 1950s and early 1960s. Since 1960 all reported new plants have used the Hoechst-Wacker technology.[4]

Direct oxidation of ethylene to form acetaldehyde is accomplished through a series of oxidation-reduction reactions. The catalyst is an aqueous solution of palladium chloride and cupric chloride. The reaction of ethylene with an aqueous palladium chloride solution to form acetaldehyde is represented by Eq. (1):

$$\underset{\text{(ethylene)}}{C_2H_4} + \underset{\text{(palladium chloride)}}{PdCl_2} + \underset{\text{(water)}}{H_2O} \longrightarrow \underset{\text{(acetaldehyde)}}{CH_3CHO} + \underset{\text{(metallic palladium)}}{Pd} + \underset{\text{(hydrochloric acid)}}{2HCl} \tag{1}$$

The palladium is reoxidized to palladium chloride by cupric chloride as shown by Eq. (2).

$$\underset{\text{(palladium)}}{Pd} + \underset{\text{(cupric chloride)}}{2CuCl_2} \longrightarrow \underset{\text{(palladium chloride)}}{PdCl_2} + \underset{\text{(cuprous chloride)}}{2CuCl} \tag{2}$$

The cuprous chloride formed is then reoxidized with oxygen or air [Eq. (3)]:

$$\underset{\text{(cuprous chloride)}}{\mathrm{2CuCl}} + \underset{\text{(oxygen)}}{\mathrm{1/2O_2}} + \underset{\text{(hydrochloric acid)}}{\mathrm{2HCl}} \longrightarrow \underset{\text{(cupric chloride)}}{\mathrm{2CuCl_2}} + \underset{\text{(water)}}{\mathrm{H_2O}} \qquad (3)$$

The net result can be represented by the overall Eq. (4):

$$\underset{\text{(ethylene)}}{\mathrm{C_2H_4}} + \underset{\text{(oxygen)}}{\mathrm{1/2O_2}} \xrightarrow[\text{(catalyst)}]{\mathrm{PdCl_2,\ CuCl_2,\ H_2O}} \underset{\text{(acetaldehyde)}}{\mathrm{CH_3CHO}} \qquad (4)$$

The process is carried out with a large excess of cupric chloride and only small "catalytic" amounts of palladium chloride. Catalyst life is practically infinite; however, HCl is consumed by side reactions and thus must be continually added.[3]

Two variations of the process have been developed. In the two-step process, air instead of oxygen is used, and ethylene and air react separately with the catalyst solution in separate reactors. In the first-stage reactor, ethylene reduces the cupric chloride catalyst by a combination of Eqs. (1) and (2). The cuprous chloride in the liquid phase is separated from the product gases and recycled with the catalyst solution to the second-stage reactor. Cuprous chloride is reoxidized [Eq. (3)] by air in the second-stage reactor and then returned to the first-stage reactor.[3]

In the single-step process a mixture of ethylene and pure oxygen reacts with the catalyst solution in a common reactor according to the reaction shown by Eq. (4). The reaction product is separated, the unreacted gas is recycled, and the consumed ethylene, oxygen, and hydrochloric acid are replaced. The single-step process has not been employed in the United States.

1. Two-Step Air-Oxidation Process[3]

a. Model Process -- The model two-step process is represented by Fig. III-1. After ethylene (Stream 1) is fed to a tubular reactor, it reacts under pressure (approximately 820 kPa at 130°C) with the catalyst solution to form acetaldehyde and cuprous chloride. The pressure of the solution (Stream 2) is reduced in a flash

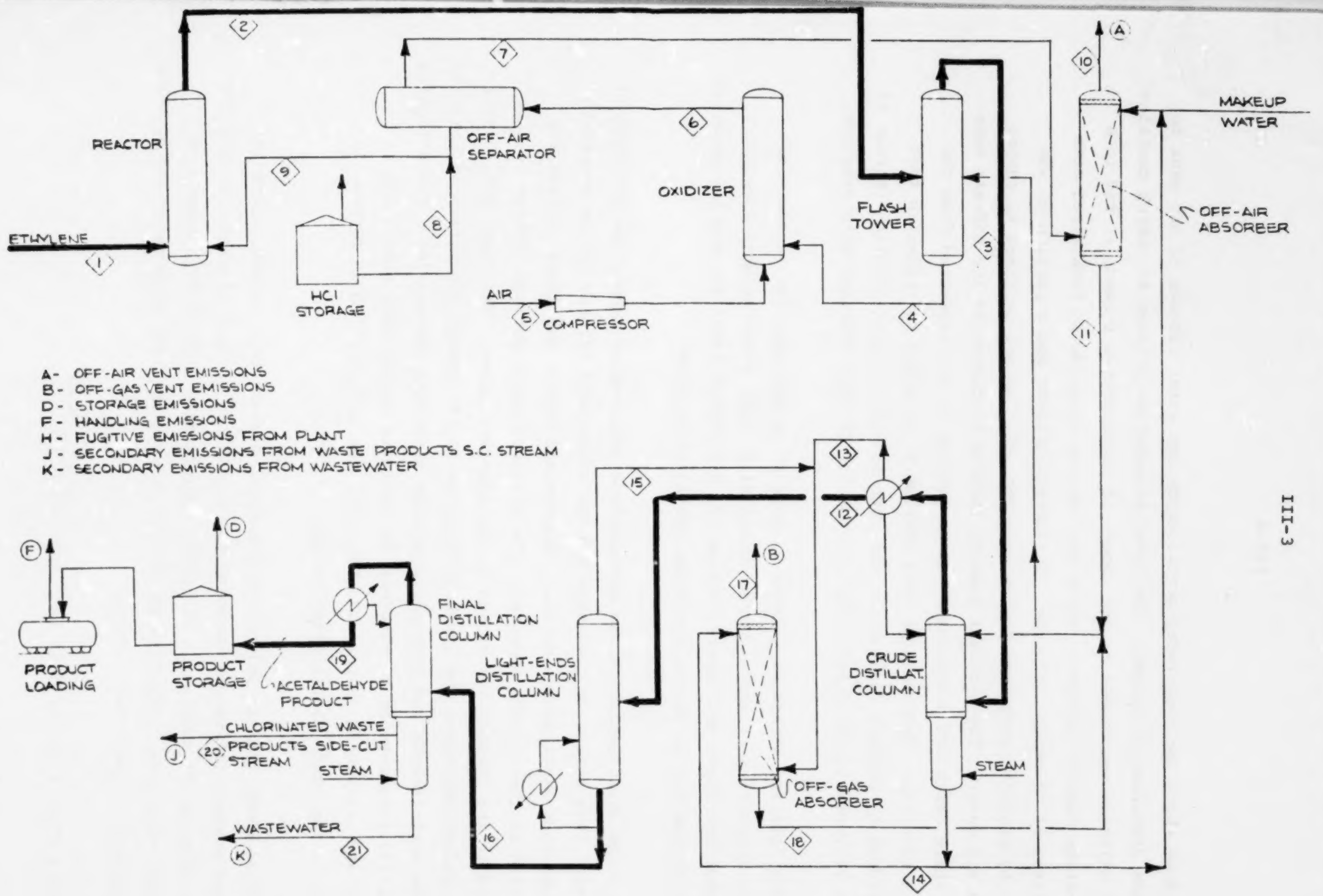

Fig. III-1. Flow Diagram for Uncontrolled Typical Plant Producing Acetaldehyde from Ethylene by Two-Step Air-Oxidation Process

tower, from which the evaporated acetaldehyde and water (Stream 3) are sent to the crude distillation column. The catalyst solution (Stream 4), which contains cuprous chloride equivalent to the amount of acetaldehyde formed, is fed to a second-stage tubular oxidizer, where the cuprous chloride is reoxidized with air (Stream 5) to cupric chloride. Unreacted ethylene and a portion of the organic by-products contained in the catalyst solution are oxidized to carbon dioxide and water. The catalyst mixture (Stream 6) passes to the off-air separator, where gases and uncondensed vapors (Stream 7) are separated from the catalyst solution. Hydrochloric acid (Stream 8) is added to replenish that lost through by-product reactions. The regenerated catalyst solution (Stream 9) is then returned to the first-stage reactor for further reaction with ethylene.

The gases from the separator (Stream 7) pass to an absorber for recovery of residual quantities of acetaldehyde, along with other water-soluble components. The unabsorbed gases and vapors (Stream 10) are vented (Vent A), and the absorber liquid (Stream 11) is fed to the crude distillation tower.

In the crude distillation column acetaldehyde and organic impurities are removed overhead. This stream is condensed and the condensate (Stream 12) is passed to the light-ends distillation column. Uncondensed vapors and gases (Stream 13) are passed to the off-gas absorber. The stripped water bottoms (Stream 14) are recycled to the reactor system and to the absorber units. The light-ends distillation column separates the low-boiling-point light-organic impurities (Stream 15) from the acetaldehyde and high-boiling-point materials (Stream 16). The off-gases (Stream 15) pass through an absorber for recovery of residual quantities of product and are vented (Stream 17, Vent B). The absorber liquid (Stream 18) returns to the crude distillation column.

The acetaldehyde (Stream 16) enters the final distillation column, where the purified product is removed overhead (Stream 19) to product storage. A side-cut stream (Stream 20) consisting of heavier chlorinated organic by-products is sometimes separated. The bottoms (Stream 21) are the remaining water and higher-boiling-point organic impurities.

Process yields of 94 to 95.2% have been reported.[3--5]

b. Process Variations -- Applications of the Hoechst-Wacker technology will result in similar plants, although process modifications are possible and are often employed. The manner of product purification may vary somewhat from that described for the model process.

A small stream of oxidized catalyst (Stream 6) is often withdrawn and passed through a separate catalyst regenerator reactor, where it is heated to about 160°C to decompose by-products.

The side-cut of chlorinated by-products (Stream 20) from the final distillation column may not be separated but instead may be combined with the wastewater for treatment and disposal.

A purge stream may be withdrawn from the absorber water circuit (Stream 14) and discharged or treated separately.

2. Single-Step Oxygen-Oxidation Process[3]

The model single-step process is represented by Fig. III-2. High-purity ethylene (Stream 1) and pure oxygen (Stream 2) are fed to the reactor filled with the catalyst solution. The reaction takes place at about 130°C and 405 kPa. Vaporized reaction products, evaporated water, and unreacted ethylene and oxygen (Stream 3) are separated from the catalyst solution (Stream 4) by the demister. A side stream of catalyst (Stream 5) is treated with oxygen and heated to about 170°C to decompose the by-products. Hydrochloric acid is continually added (Stream 6) to replenish that lost through by-product reactions.

The reaction products (Stream 3) are quenched and then passed to the absorber, where acetaldehyde vapors are cooled and absorbed with water to separate it from the unreacted gases. The major portion of the gas is recycled (Stream 7) to the reactor, and a small amount (Stream 8) is vented (Vent A) to prevent accumulation of gaseous contaminants. The crude acetaldehyde solution (Stream 9) from the bottom of the absorber is passed to the extractive distillation column, where the acetaldehyde solution (Stream 10) is separated from the low-boiling-point light-organic components (Stream 11) by extractive distillation with water. The off-gases from the column overhead are vented (Vent B).

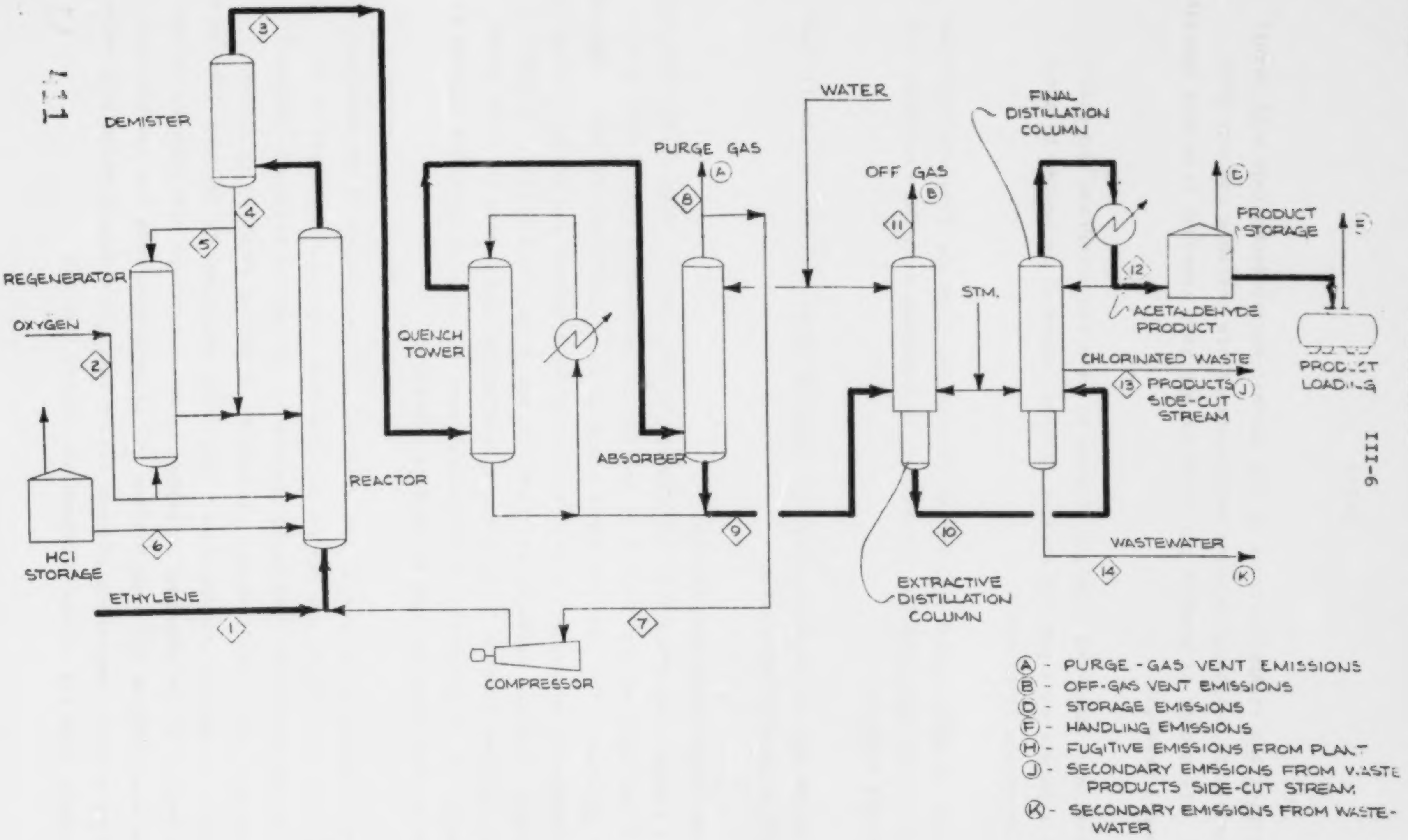

Fig. III-2. Flow Diagram for Uncontrolled Typical Plant Producing Acetaldehyde from Ethylene by Single-Step Oxygen-Oxidation Process

Acetaldehyde (Stream 12) is separated from water and purified in the final distillation column. A side-cut stream is taken to partially withdraw the high-boiling chlorinated by-products (Stream 13), and those remaining are discharged with the wastewater (Stream 14). Process yeild is reported to be 94 to 95.2%.[3--5]

3. Process Comparison

The first-stage reactor of the two-step process operates at a significantly higher pressure than that in the single-step process, which results in a higher reaction rate and makes it possible for a single-pass operation to be used.[4] Since the gases are not recycled, ethylene can be used that is considerably lower in purity than is necessary for the single-step process.[3] The process yields (kg of acetaldehyde produced per kg of pure ethylene fed to the reactor) are reported to be equal for both processes.[3--5]

In the two-step process emissions from vent A consist primarily of inert gas (99%) since the process uses air for the oxygen supply and nearly all of the oxygen is consumed. The volume of the single-step process from vent A is very small and consists mostly of VOC since pure ethylene and oxygen are fed to the reactor. The total amount of ethylene lost is essentially the same with each process.

The two-step process produces relatively small amounts of heavily contaminated wastewater, since most of the water is removed in the crude distillation step and recycled. The single-step process produces considerably larger amounts of dilute wastewater since the water used in absorption of the product is discharged on final product purification.

Published data indicate that the single-step process consumes 4 g of HCl per kg of acetaldehyde produced, whereas the two-step process consumes 15 g/kg.[3] If it could be concluded from these data that less chlorinated by-product waste material is produced by the single-step process than by the two-step process, the single-step process would be more attractive from an environmental standpoint.

The economics of the two processes are similar, with the oxygen-based single-step process having better economy for smaller plants (less than 100 Gg/yr) and the air-based two-step process having the advantage for large plants (greater than 100 Gg/yr).[3]

C. ACETALDEHYDE FROM ETHANOL

Before the Hoechst-Wacker ethylene-based process was developed, acetaldehyde was produced principally by the catalytic oxidation of ethanol.[4] Preheated air and alcohol vapors are passed over a silver catalyst at 480°C to produce acetaldehyde according to the following equation:[2]

$$\underset{\text{(ethanol)}}{CH_3CH_2OH} \quad + \quad \underset{\text{(oxygen)}}{1/2O_2} \quad \longrightarrow \quad \underset{\text{(acetaldehyde)}}{CH_3CHO} \quad + \quad \underset{\text{(water)}}{H_2O}$$

Heat generated by the reaction is used for producing steam. The reaction gases are scrubbed with ethanol to recover the product and with water to remove soluble components before they are discharged. The off-gas contains mainly nitrogen and hydrogen and can be flared or thermally oxidized. Acetaldehyde is separated and purified in a finishing column. The column bottoms, containing largely unreacted ethanol and water, go to an ethanol recovery column, where ethanol is recovered and then returned to the process. Wastewater containing higher-boiling reaction by-products is discharged as the column bottoms. Yields of 97% have been reported.[6]

No new ethanol-based plants have been built since the ethylene-based process was developed.[4]

D. ACETALDEHYDE FROM ACETYLENE[2]

Acetylene-based processes have been used to produce acetaldehyde commercially since 1917. The ethylene-based process, however, has completely replaced acetylene as a commercially important process. The acetylene process involved passing high-purity acetylene under pressure through a reactor containing a mercury catalyst dissolved in 18 to 25% sulfuric acid at 70 to 90°C. Acetaldehyde is formed by the following reaction:

$$\underset{\text{(acetylene)}}{HC{\equiv}CH} \quad + \quad \underset{\text{(water)}}{H_2O} \quad \underset{\text{(catalyst)}}{\xrightarrow[H_2SO_4]{Hg^{2+}}} \quad \underset{\text{(acetaldehyde)}}{CH_3CHO}$$

E. ACETALDEHYDE FROM SATURATED HYDROCARBONS[2]

Acetaldehyde is formed as a coproduct in the vapor-phase oxidation of saturated hydrocarbons, such as butane. This process was of significant commercial importance in the United States until it was rendered uncompetitive by rising costs of petroleum-based feedstocks. Oxidation of butane yields acetaldehyde, formaldehyde, methanol, acetone, and mixed solvents as major products; other aldehydes, alcohols, ketones, glycols, acetals, epoxides, and organic acids are formed in smaller concentrations. The cost of feedstocks and problems in product separation and recovery make it unlikely that new plants will be built based on this process.

F. ACETALDEHYDE FROM SYNTHESIS GAS[2]

A process for converting synthesis gas directly to acetaldehyde in a single step using a rhodium catalyst was reported in 1974. Synthesis gas is passed over a 5% rhodium on a silicon oxide catalyst bed at a temperature of 300°C and a pressure of 2000 kPa to form acetaldehyde by the following equation:

$$\underset{\text{(carbon monoxide)}}{CO} + \underset{\text{(hydrogen)}}{H_2} \xrightarrow[\text{(catalyst)}]{} \underset{\text{(acetaldehyde)}}{CH_3CHO} + \text{other products}$$

The principal coproducts formed are acetaldehyde, 24%; acetic acid, 20%; and ethanol, 16%.

G. REFERENCES*

1. 1978 Directory of Chemical producers, United States of America, Chemical Information Services, Stanford Research Institute, Menlo Park, CA, p. 415.

2. H. J. Hagemeyer, "Acetaldehyde," pp. 97--112 in Kirk-Othmer Encyclopedia of Chemical Technology, 3d ed., vol. 1, edited by M. Grayson et al., Interscience, New York, 1978.

3. R. Jira, W. Blau, and D. Grimm, "Acetaldehyde Via Air or Oxygen," Hydrocarbon Processing 55(3), 97--100 (March 1976).

4. P. L. Morse, Acetaldehyde, Report No. 24, A private report by the Process Economics Program, pp. 3 and 10, Stanford Research Institute, Menlo Park, CA (April 1967).

5. Hoechst-Uhde Corp., "Acetaldehyde from Ethylene (Aldehyd GmbH)," Chemical Week 46(11) 135 (1967).

6. Veba-Chemie AG, "Acetaldehyde," Hydrocarbon Processing 56(11), 118 (1977).

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*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals are photochemically unreactive. However, many photochemically unreactive organic chemicals are of concern and may not be exempt from regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. ACETALDEHYDE FROM ETHYLENE BY THE TWO-STEP AIR-OXIDATION PROCESS

1. Typical Plant

The typical plant for this study has a capacity of 113.5 Gg/yr, based on 8760 hr of operation per year. Although not an actual operating plant, it is typical of existing plants. The plant utilizes the model two-step process (Fig. III-1) and fits today's acetaldehyde manufacturing and engineering technology for that process.

The Celanese Clear Lake, TX, plant and the Texas Eastman Longview, TX, plant have two production units each with reported capacities of about 113.5 Gg/yr per unit. The Celanese Bay City plant has one unit with a reported capacity of 136 Gg/yr (see Table II-2). Foreign plants based on ethylene have capacities ranging from 21.8 to 134.3 Gg/yr.[1]

2. Sources and Emissions

Uncontrolled emission rates and sources for the model plant are summarized in Table IV-1 and are described below. The process emission rates are in the range of actual emission data reported by existing plants.[2--4] The off-air and off-gas absorbers (scrubbers) for the purpose of this report are considered to be integral components of process equipment important to the efficiency of the process and not emission control devices as such. Potential storage, handling, and fugitive emissions were calculated from characteristics of the model process that were based on data on existing plants.[2--4]

Table IV-1. Total VOC from Uncontrolled Emissions Produced by Model Plant Using Two-Step Air-Oxidation Process

Emission Source	Stream Designation (Fig.III-1)	Emissions	
		Ratio[a] (g/kg)	Rate (kg/hr)
Off-air absorber vent	A	2.27	29.4
Off-gas absorber vent	B	2.79	36.1
Intermittent[b]	B	0.005	0.06
Storage	D	0.17	2.3
Handling	F	0.47	6.1
Fugitive	H	0.58	7.5
Secondary	J,K	[c]	[c]

[a] g of total VOC per kg of acetaldehyde produced.

[b] Average rate for entire year, based on one startup per year.

[c] Secondary emissions were not calculated; potential for significant secondary emissions exists.

a. Off-Air Vent Emissions -- The off-air absorber vent (Vent A, Fig. III-1) is a principal source of emissions from the acetaldehyde production plant. Nitrogen and other inert or unreacted components of the air fed to the second-stage reactor and gases or unabsorbed vapors generated in the catalyst oxidation or regeneration process are discharged from this vent. The VOC components, principally acetaldehyde, methyl chloride, and ethyl chloride, amount to only 0.15 wt % of the total flow from this vent. The compositions of the model-plant uncontrolled emissions are given by Table IV-2. The average emission during normal operation is given in Table IV-1. The estimated flow from this vent is 271 m^3/min.

b. Off-Gas Vent Emissions -- The off-gas vent (Vent B, Fig. III-1) discharges gases and low-boiling-point VOC vapors separated in product purification operations. The VOC components (see Table IV-2) make up 4.8 wt % of the total discharge from this vent. The average emission during normal operation is given in Table IV-1. The estimated flow from this vent is 8.9 m^3/min.

c. Intermittent Air Emissions -- The acetaldehyde plant is normally operated continuously and is shut down for annual maintenance. During startup the amount of ethylene in the off-gas (Vent B) may run as high as 25 to 50% for 2 to 6 hr.[3] After the catalyst is activated, the ethylene content decreases to normal levels. The intermittent emissions reported in Table IV-1 were calculated based on one startup per year.

d. Fugitive Emissions -- Process pumps and valves are potential sources of fugitive emissions. The model plant is estimated to have 19 pumps handling VOC, with 12 used for light-liquid service and 7 for heavy-liquid service. The model plant is estimated to have 648 process valves handling VOC, with approximately 30% used for heavy-liquid service, 50% for light-liquid service, and 20% for gas/vapor service. The model plant is estimated to have 16 relief valves, with approximately 80% used for gas/vapor service and 20% for light-liquid service. The fugitive-emission factors from Appendix B were applied to determine the fugitive emissions shown in Table IV-1.

e. Storage and Handling Emissions -- Emissions result from the storage and handling of acetaldehyde. Sources for the model plant are shown in Fig. III-1. Not shown on the process flow diagram are surge tanks and catalyst, crude aldehyde,

Table IV-2. Uncontrolled Emission and Waste Composition for Model Two-Step Process

		Emission Ratio (g/kg)[a]		Waste Discharge Ratio (g/kg)[b]	
Component	Formula	Vent A Off-Air	Vent B Off-Gas	Discharge K Wastewater	Discharge J Side Cut
VOC					
Ethylene	C_2H_4		1.00		
Acetaldehyde	C_2H_4O	1.47	0.19		7.8
Methyl chloride	CH_3Cl	0.76	0.37		
Ethyl chloride	C_2H_5Cl	0.04	0.78		
Methylene chloride	CH_2Cl_2		0.10		
Chloroform	$CHCl_3$		0.35		
Acetic acid	$C_2H_4O_2$			13.9	0.6
Chloroacetaldehyde	C_2H_3OCl				5.5
Acetyl chloride	$C_2H_2OCl_2$			4.2	5.0
Chloral	C_2HOCl_3			2.1	3.4
Paraldehyde	$(C_2H_4O)_3$			1.6	
Other organic				4.0	2.0
Total VOC		2.27	2.79	25.8	24.3
Other gases					
Carbon dioxide	CO_2	37.75	22.65		
Nitrogen	N_2	1430.55	30.15		
Oxygen	O_2	11.67	0.50		
Argon	A	24.39	0.67		
Total other gases		1504.36	53.79		
Water	H_2O	1.79	0.82	795.6	25.5
Total stream		1508.44	57.58	821.4	49.8

[a] g of off-air or off-gas per kg of acetaldehyde.

[b] g of discharge K or J per kg of acetaldehyde.

and process-water storage tanks. These tanks are operated at positive pressure and are vented back to the process and therefore do not contribute to the storage emissions. Emissions from the storage of the side-cut organic by-products (Discharge J) and/or wastewater (Discharge K) are considered under secondary emissions.

The low boiling point and relatively high vapor pressure of acetaldehyde require that it be stored and handled in pressurized tanks, which are padded with nitrogen. The model plant has three 1079-m^3 spherical storage tanks 12.8 m in diameter. The tanks are maintained at ambient temperature and between 207 and 377 kPa pressure. The calculated average storage emissions based on 45 turnovers per year are given in Table IV-1.

All of the acetaldehyde produced in the model plant is shipped in pressurized tank cars. In the uncontrolled plant, tank cars are vented before they are filled. During filling, the tank car is vented back to the acetaldehyde storage tank. The calculated handling emission from the tanks being vented before they are filled is given in Table IV-1.

f. Secondary Emissions -- The model plant discharges approximately 10.6 m^3 of process wastewater per hour that contains 334-kg/hr VOC (Discharge K, Fig. III-1) and approximately 0.6 m^3 of chlorinated by-product waste per hour that contains 315-kg/hr VOC (Discharge J). These streams can be significant sources of secondary emissions resulting from desorption or evaporation before they are ultimately treated and disposed of. Probable secondary emissions were not calculated.

B. ACETALDEHYDE FROM ETHYLENE BY THE SINGLE-STEP OXYGEN-OXIDATION PROCESS

There are no acetaldehyde plants in the United States employing the single-step oxidation process; thus no actual emission data could be obtained. The following inferences are based on a comparison of the process chemistry, model process flow sheets, and published data pertaining to the two processes.

1. Sources and Emissions

The process yields reported for both processes are equal,[5--7] which indicates nearly equal amounts of total carbon content in the air emissions, wastewater, and by-products generated by each process. The amount of HCl consumed by the two-step process is reported to be 2.6 to 3.7 times that used by the single-step process.[5,7] This indicates that fewer chlorinated by-products are generated by the single-step process.

2. Purge-Gas Vent Emissions

The purge-gas vent (Vent A, Fig. III-2) is required to purge contaminants from the recycle gas stream. The volume of the vent stream should be relatively small, depending on the level that contaminates can be tolerated in the reaction system. Since high-purity oxygen and ethylene are fed to the reactor, the purge stream contains principally unreacted ethylene, acetaldehyde, by-product carbon dioxide, and water vapor, together with small quantities of oxygen, argon and nitrogen from the oxygen feed, ethane from the ethylene feed, and chlorinated by-product compounds. The concentration and quantity of total VOC (ethylene and acetaldehyde plus the chlorinated compounds) discharged from this vent are expected to be relatively high.

3. Off-Gas Vent Emissions

The off-gas (Vent B, Fig. III-2) discharges the low-boiling-point light organic by-products separated from the process stream during product purification. The vent stream volume would be expected to be small, containing largely chlorinated by-products and small quantities of ethylene, acetaldehyde, and inert gases.

4. Secondary Emissions

Since water absorption is used for separating the crude product from the recycle gas stream, the quantity of wastewater discharged would be much higher than that reported for the two-step process. The VOC contained in the water, however, would be less than that of the two-step process since less by-product waste is produced. The potential for secondary emissions therefore should be less.

5. Other Emissions

The intermittent, fugitive, and storage and handling emissions are expected to be similar to those of the two-step process.

C. REFERENCES*

1. P. L. Morse, Acetaldehyde, pp. 15 and 16 in Report No. 24, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (April 1967).

2. J. J. Cudahy and J. F. Lawson, IT Enviroscience, Inc., Trip Report to Celanese Plant, Celanese Chemical Co., Clear Lake City, TX, Sept. 22, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. J. J. Cudahy and J. F. Lawson, IT Enviroscience, Inc., Trip Report to Texas Eastman Plant, Texas Eastman Chemical Co., Longview, TX, Nov. 16, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. P. E. Hime, Celanese Chemical Co., response to Texas Air Control Board 1975 Emissions Inventory Questionnaire for Celanese Chemical Co., Bay City, TX, Plant, Mar. 19, 1976.

5. R. Jira, W. Blau, and D. Grimm, "Acetaldehyde Via Air or Oxygen," Hydrocarbon Processing 55(3), 97--100 (March 1976).

6. P. L. Morse, Acetaldehyde, pp. 3 and 10 in Report No. 24, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (April 1967).

7. Hoechst-Uhde Corp., "Acetaldehyde from Ethylene (Aldehyd GmbH)," Chemical Week 46(11), 135 (1967).

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V. APPLICABLE CONTROL SYSTEMS

A. ACETALDEHYDE FROM ETHYLENE BY THE TWO-STEP AIR-OXIDATION PROCESS

1. Off-Air Vent Emissions

The emissions from the off-air vent (Vent A) remain uncontrolled for the typical plant. The total flow from this vent is 16,275 m^3/hr (19,527 kg/hr), containing 29.4-kg/hr, or 0.15 wt %, VOC. The stream contains less than 0.8 wt % oxygen, with the bulk of the emission being nitrogen gas (see Table IV-2).

Typical of existing plants in the United States,[1--3] a water scrubber (absorber) is employed to recover residual amounts of acetaldehyde from the off-air stream before it is vented. These scrubbers are operated under high pressure, and chilled water is used to achieve maximum absorption efficiency.

The gases vented are estimated to have a heating value of approximately 37 kJ/m^3. A minimum heating value of "115 Btu/ft^3" (ref. 4) (4300 kJ/m^3) is required to successfully flare the gas.[4] Thus the use of a flare or other thermal oxidation control devices for destruction of the residual VOC in this stream would require very large amounts of auxiliary fuel. Combining this stream with the emission stream from vent B would raise the heating value to only about 90 kJ/m^3. Emissions from the scrubber off-air are not controlled in existing plants or in the typical plant described (see Table V-1).

2. Off-Gas Vent Emissions

The emissions from the typical plant off-gas vent (Vent B) are controlled by a flare. An emission reduction of 99%, typical of emission reductions achieved by a properly designed flare,[5] was used to calculate the controlled emission rate given in Table V-1. Usually the ethylene feedstock is produced on-site in an adjacent plant. The flare system associated with the ethylene plant might be used jointly for both the ethylene and the acetaldehyde plants.

The total flow from vent B of the typical plant is 531 m^3/hr (743 kg/hr) and contains about 36-kg/hr, or 4.8 wt %, VOC. The heating value of the mixture is about 1735 kJ/m^3. Flaring of this emission requires that about 45-m^3/hr natural gas be added for minimum combustion conditions to be achieved. Flaring produces undesirable HCl emissions.

Table V-1. Total Controlled VOC Emissions for Typical Plant Using Two-Step Air-Oxidation Process

Emission Source	Stream Designation (Fig.III-1)	Control Device or Technique	Emission Reduction (%)	Emissions Ratio[a] (g/kg)	Emissions Rate (kg/hr)
Off-air absorber vent	A	None		2.27	29.4
Off-gas absorber vent	B	Flare	99	0.03	0.36
Intermittent[b]	B	Flare	99	Negligible	Negligible
Storage	D	Recycle	100	Negligible	Negligible
Handling	F	Recycle	99	0.005	0.06
Fugitive	H	Repair and maintenance	91	0.2	2.6
Secondary	J,K	c	c	c	c

[a] g of total VOC per kg of acetaldehyde produced.

[b] Intermittent startup emissions are discharged from vent B, which is controlled by a flare.

[c] Secondary emissions and emission control measures were not defined.

A thermal oxidation system with heat recovery is a possible control alternative. Although auxiliary fuel would be required to maintain stable combustion, thermal oxidation would produce emission reduction efficiencies of greater than 99%. Combustion of the mixture, however, produces acid gas emissions, which must be considered in design of the equipment. Thermal oxidizer systems and efficiencies are discussed in a separate EPA document.[6]

3. Intermittent Air Emissions

Intermittent high emissions from vent B produced during plant startup are reduced by 99% by the flare system used for control of emissions from vent B (see Table V-1). A flare system is ideally suited for burning vent streams of widely varying quantity and composition. If a thermal oxidation system with heat recovery were used to control emissions from vent B, the increased heat rate during startup could be a problem in sizing and operation of the oxidation system.

4. Fugitive Sources

Controls for fugitive sources are discussed in a separate EPA document covering fugitive emission from the synthetic organic chemicals manufacturing industry. Control of emission from the pumps and valves can be attained by an appropriate leak detection system followed by repair maintenance. Controlled fugitive emissions have been calculated with the factors given in Appendix B and are included in Table V-1. The factors are based on the assumption that major leaks are detected and repaired.

5. Storage and Handling Sources

In the typical plant acetaldehyde storage emissions are controlled by the discharge from the storage-tank pressure-relief valves being returned to the off-gas absorber. Emissions from the absorber (Vent B) are flared, which results in an overall reduction of essentially 100% (see Table V-1).

Handling emissions from the venting of incoming empty tank cars are controlled by venting to the off-gas absorber. While the tank cars are being filled they are vented back to the acetaldehyde storage tank. A control efficiency of 99% obtained with the absorber system was used to calculate the controlled emissions given in Table V-1.

6. Secondary Emissions

Secondary emissions can result from evaporation of VOC contained in aqueous wastes going to wastewater treatment (Discharge K) and from processing or disposal of the side-cut by-products (Discharge J). Considerable potential exists for large secondary emissions because of the quantity and concentration of VOC contained in these streams. Some form of pretreatment would be required to lower the organic concentration of the wastewater stream before it is to be treated by conventional biodegradation.[7] Side-cut organics can be incinerated.[7] One plant disposes of both streams in a deep-well system.[1] Control of secondary emissions will be discussed in a future EPA report.

B. ACETALDEHYDE FROM ETHYLENE BY THE SINGLE-STEP OXYGEN-OXIDATION PROCESS

No acetaldehyde plants using the single-step oxidation process have been built in the United States; thus no data are available on the emissions and/or emission controls used.

Emissions from the purge-gas vent (Vent A) should have sufficient heating value to permit control by flaring or other forms of thermal oxidation. Emissions from vent B and intermittent, storage and handling, and fugitive emissions should be controllable by the same measures used in the two-step process. Secondary emissions from the single-step process are less of a problem since there are fewer by-products formed and the wastewater is rather dilute and treatable by biological degradation.[7]

C. CONTROL MEASURES CURRENTLY USED

The emission control measures now in effect in domestic acetaldehyde plants are discussed in Appendix C.

D. REFERENCES*

1. J. J. Cudahy and J. F. Lawson, IT Enviroscience, Inc., Trip Report for Celanese Plant, Celanese Chemical Company, Clear Lake City, TX, Sept. 22, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. J. J. Cudahy and J. F. Lawson, IT Enviroscience, Inc., Trip Report for Texas Eastman Plant, Texas Eastman Chemical Co., Longview, TX, Nov. 16, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. P. E. Hime, Celanese Chemical Co., response to Texas Air Control Board 1975 Emissions Inventory Questionnaire for Celanese Chemical Co., Bay City, TX Plant, March 19, 1976.

4. J. F. Straitz, III, "Make the Flare Protect the Environment," Hydrocarbon Processing **56**(10), 134 (1977).

5. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

6. J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

7. R. Jira, W. Blau, and D. Grimm, "Acetaldehyde Via Air or Oxygen," Hydrocarbon Processing **55**(3), 97--100 (March 1976).

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APPENDIX A

Table A-1. Properties of Acetaldehyde, Methyl Chloride, Ethyl Chloride, and Chloroform

	Acetaldehyde[a]	Methyl Chloride[b]	Ethyl Chloride[c]	Chloroform[d]
Synonyms	Acetic aldehyde, ethyl aldehyde	Chloromethane	Chloroethane, muriatic acid	Trichloromethane
Molecular formula	C_2H_4O	CH_3Cl	C_2H_5Cl	$CHCl_3$
Molecular weight	44.05	50.49	64.52	119.39
Physical state	Clear liquid	Gas	Liquid or gas	Liquid
Density	0.7834 g/ml at 18°C	0.9159 at 20°C/4°C	0.8978 at 20°C/4°C	1.4984 at 15°C
Vapor pressure	1.23 atm at 25°C	2.83 atm at 25°C	20 mm at 21°C	200 mm at 25.9°C
Vapor specific gravity	1.52	1.78	2.22	4.12
Boiling point at 1 atm	20.8°C	-24.2°C	12.3°C	61.26°C
Water solubility	Infinite	4.9 g/liter	5.7 g/liter	8.0 g/liter

[a] From: J. Dorigan et al., "Acetaldehyde", p. AI-6 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C), Rev. 1, Appendix I, MTR-7248, MITRE Corp., McLean, VA (September 1976).

[b] "Methyl Chloride" ibid. (Chemicals F-N), p AIII-174.

[c] "Ethyl Chloride," ibid. (Chemicals D-E), p AII-254.

[d] "Chloroform," ibid. (Chemicals A-C), p A AI-265.

APPENDIX B

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX C

EXISTING PLANT CONSIDERATIONS

Table C-1 lists process control devices reported to be in use by industry. To gather information for the preparation of this report site visits were made to manufacturers of acetaldehyde (AcH). Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Research Triangle Park, NC.[1,2]

A. PROCESS EMISSIONS FROM EXISTING PLANTS[1]

1. Celanese Chemical Co., Clear Lake, TX

The acetaldehyde production facility consists of two identical continuous trains of equipment to produce acetaldehyde by the two-stage process for air oxidation of ethylene. The total published capacity of the Celanese Clear Lake, TX, acetaldehyde plant is 500 million pounds per year. The process was licensed from Aldehyde GmbH, a jointly owned company formed by Hoechst, A. G. and Wacker-Chemie GmbH. The trains were built in 1967 and 1971.

Emissions from the process can be from two sources: the high-pressure vent absorber and the low-pressure vent absorber. Emission compositions and flow data were reported in Table C-2.

The methane and ethane concentrations in these streams are mainly from the methane used as an inert-gas blanket on the acetaldehyde storage tanks. Methane padding is no longer used and consequently the methane and ethane concentrations in the low-pressure vent absorber vent gas will be much lower than that shown.

Both the high-pressure and low-pressure vent absorbers are used for product recovery and are very important for process efficiency. The low-pressure vent absorber is also fed an organic stream from the light-ends column and a scrubbing water stream from the finishing column bottoms, as well as vent streams from the process, the acetaldehyde storage tanks, and the acetaldehyde tank car loading systems. The unabsorbed vent gases from the low-pressure vent absorber are fed to a process flare. The vent gas from both acetaldehyde process trains accounts for about 70 to 80% of the load to this flare.

Table C-1. Control Methods Currently Used by the Domestic Acetaldehyde Industry[a]

	Control Methods For					
Company and Location	Off-Air[b] Vent	Off-Gas[b] Vent	Product Storage	Product Handling	Side-Cut Organics	Wastewater
Celanese Bay City, TX	None	Flare	Recycle	Recycle	[c]	[c]
Celanese Clear Lake City, TX	None	Flare	Recycle	Recycle[d]	Deep well[e]	Deep well
Texas Eastmen Longview, TX	None	None	Recycle	Recycle	[c]	[f]

[a] For those plants producing acetaldehyde from ethylene by the two-step air-oxidation process; see Table II-2.

[b] The off-air and off-gas absorbers (scrubbers) for the purpose of this report are considered as integral components of process equipment and not as emission controls as such.

[c] Not reported.

[d] Empty tank cars are vented to a flare before they are refilled.

[e] Combined with wastewater.

[f] Specific data not reported; wastewater from the Longview facility goes to anerobic lagoons.

Table C-2. High- and Low-Pressure Scrubber Emissions from Celanese Plant

Waste Gas	Emissions (wt %)	Emissions (lb/1000 lb of AcH)
	High Pressure Scrubber Emissions (Off-Air Vent)	
C_2H_4O	0.3	4.3
H_2O	0.2	2.7
N_2	95.3	1,540.2
O_2	1.9	30.9
CO_2	2.3	37.8
	100.0	1,615.9
	Low Pressure Scrubber Emissions (Off-Gas Vent)	
C_2H_4	0.9	0.5
CH_3Cl	1.9	1.1
C_2H_5Cl	2.1	1.1
CH_2Cl_2	0.3	0.1
$CHCl_3$	0.7	0.4
N_2	37.5	20.6
O_2	0.9	0.5
CO_2	41.9	23.0
CH_4	11.9	6.5
C_2H_6	2.9	1.6
	101.0	55.4

2. Texas Eastman, Longview, TX[2]

The Texas Eastman acetaldehyde production facility at Longview was also licensed from Aldehyde GmbH and with regard to process emissions appears essentially identical to the Celanese acetaldehyde production facility at Clear Lake, TX.

Typical emissions data reported for the Texas Eastman facility are given in Table C-3.

Both scrubbers recover product and are very important for process efficiency. Vent streams from process and product storage plus tank car loading emissions are also directed to the low-pressure scrubber. No additional control device is used for control of emissions from the high- and low-pressure scrubbers.

B. TOTAL INDUSTRY EMISSIONS

Table C-4 lists the estimated emissions for the acetaldehyde industry for 1979. This estimate is based on emission data received from the major acetaldehyde producers[1,2] and/or emission rates calculated for the typical plant. It is estimated that the total emissions from all plants during 1979 were approximately 1.1 Gg.

The emissions from these plants would have been 2.4 Gg during 1979 if they had been uncontrolled.

C. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

Table C-3. High- and Low-Pressure Scrubber Emissions from Texas Eastman Plant

Waste Gas	Emissions (lb/hr)	Emissions (vol %)
	High-Pressure Scrubber Emissions (Off-Air Vent)	
C_2H_4O	1	0.0017
CH_3Cl	20	<0.05
CO_2	457	0.8
N_2	37,668	97.8
C_2H_5Cl	<100	<0.2
H_2O	47	0.2
Argon	649	1.2
	Low-Pressure Scrubber Emissions (Off-Gas Vent)	
C_2H_4	5	0.3
CO_2	741	27.8
N_2	1,158	68.3
C_2H_4O	<2	<0.1
CH_3Cl	6	0.2
C_2H_5Cl	24	0.7
H_2O	21	1.9
Argon	20	0.8

Table C-4. Estimated 1979 Acetaldehyde Industry Emissions

Source	Total VOC Emissions[a] (Gg/yr) Uncontrolled[b]	Total VOC Emissions[a] (Gg/yr) Current Controlled[c]
Off-air vent A	0.745	0.745
Off-gas vent B	1.119	0.240
Storage	0.077	Neg
Handling	0.208	0.001
Fugitive	0.253	0.128
Secondary	d	d
Total	2.402	1.114

[a] Based on estimated total 1978 production of 448 Gg.

[b] Based on uncontrolled emissions reported by industry and/or emission rates calculated for uncontrolled typical plant (Table IV-1).

[c] Current control represents the degree of emission control obtained by industry in 1976, based on control measures reported by industry (Table C-1) and the control efficiencies described for typical plant controls (Table V-1).

[d] Available data insufficient to estimate secondary emissions; however, it is believed that secondary emissions are currently small because of control measures taken by industry.

D. REFERENCES*

1. J. J. Cudahy and J. F. Lawson, IT Enviroscience, Inc., Trip Report for Celanese Plant, Celanese Chemical Company, Clear Lake City, TX, Sept. 22, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. J. J. Cudahy and J. F. Lawson, IT Enviroscience, Inc., Trip Report for Texas Eastman Plant, Texas Eastman Chemical Co., Longview, TX, Nov. 16, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. A. K. Rafie and L. S. Soder, "Acetaldehyde--Product Review," p 601.5020I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (March 1979).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 7

ETHANOLAMINES

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Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

February 1980

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D52E

CONTENTS OF REPORT 7

	Page
I. ABBREVIATIONS AND CONVERSION FACTORS	I-1
II. INDUSTRY DESCRIPTION	II-1
A. Introduction	II-1
B. Ethanolamines Usage and Growth	II-1
C. Domestic Producers	II-1
D. References	II-5
III. PROCESS DESCRIPTIONS	III-1
A. Introduction	III-1
B. Ethanolamines from Ethylene Oxide and Ammonia	III-1
C. Process Variation	III-3
D. References	III-4
IV. EMISSIONS	IV-1
A. Emissions	IV-1
B. References	IV-3
V. IMPACT ANALYSIS	V-1
A. Industry	V-1
B. References	V-2

APPENDICES OF REPORT 7

	Page
APPENDIX A. PHYSICAL PROPERTIES OF ETHANOLAMINES	A-1

TABLES OF REPORT 7

Number		Page
II-1	Usage of Ethanolamines	II-2
II-2	Ethanolamines Capacity	II-3
A-1	Physical Properties of Ethanolamines	A-1

FIGURES OF REPORT 7

Number		Page
II-1	Locations of Plants Manufacturing Ethanolamines	II-4
III-1	Production of Ethanolamines by the Ethylene Oxide—Ammonia Process	III-2

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

Ethanolamines production was chosen for study as part of the family of products produced from ethylene oxide and because preliminary estimates indicated that emissions of volatile organic compounds (VOC) were relatively high. This study is presented as an abbreviated product report because information from producers indicates that process VOC emissions are negligible.

Three ethanolamine products were studied: monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA). They are low-vapor-pressure colorless liquids at room temperature or slightly above. Physical property data are given in Appendix A.

B. ETHANOLAMINES USAGE AND GROWTH

Table II-1 gives a breakdown of the use of ethanolamines. In 1978 the demand for ethanolamines was 165 Gg. The production ratio in recent years has been 32% MEA, 31% DEA, and 37% TEA.[1] MEA is used mainly for scrubbing acid gases from gas streams, DEA is used chiefly in fatty alkanolamides for liquid detergents and textile chemicals, and TEA is used in the production of fatty acid soaps for dry cleaning and in cosmetics.[2]

Through 1983 ethanolamine consumption is expected to increase at the rate of 3% per year; no significant new markets are expected.[1] The availability and cost of ethanolamines depend on the availability and cost of the raw materials ethylene oxide and ammonia. All the domestic producers have captive ethylene oxide production.[2]

C. DOMESTIC PRODUCERS

As of early 1979 there were four domestic producers of ethanolamines in five different locations.[1] Table II-2 lists the producers and their rated capacities. Figure II-1 shows the plant locations. Dow Chemical started up the Plaquemine, LA, facility with a rated capacity of 56.7 Gg/yr; they mothballed a facility in Freeport, TX, that had a capacity of 22.7 Gg/yr. The Freeport plant is not likely to reopen.[1] In 1979 Jefferson Chemical started up a new plant in Port Neches, TX, with a rated capacity of 68 Gg/yr.[1]

Table II-1. Usage of Ethanolamines*

End Use	Percent of Total Usage
Detergents (textile, toilet goods, metal and other specialty surfactants)	40
Gas conditioning and petroleum use	25
Other (including agricultural intermediates and cement grinding aids)	15
Export	20

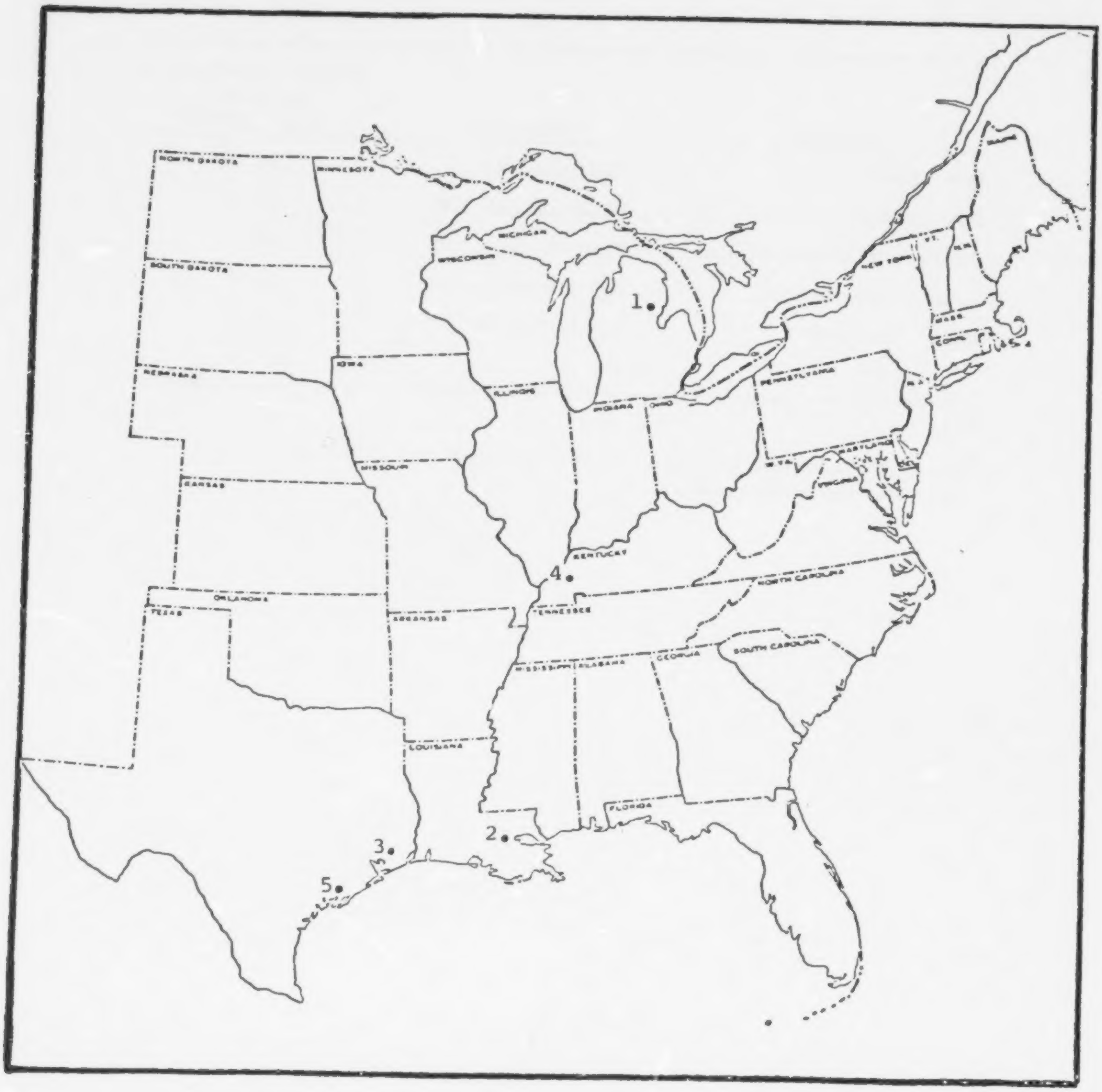
*See ref. 1.

Table II-2. Ethanolamines Capacity[a]

Company	Location	Annual Production Capacity (Gg) (1979)
Dow Chemical Co.	Midland, MI	22.7[b]
Dow Chemical Co.	Plaquemine, LA	56.7
Jefferson Chemical Co.	Port Neches, TX	68.1
Olin Chemical Co.	Brandenburg, KY	13.6
Union Carbide	Seadrift, TX	104.3
Total		265.4

[a] See ref. 1.

[b] This unit mostly produces isopropanolamines but can also produce ethanolamines.



1. Dow Chemical Co., Midland, MI
2. Dow Chemical Co., Plaquemine, LA
3. Jefferson Chemical Co., Port Neches, TX
4. Olin Chemical Co., Brandenburg, KY
5. Union Carbide, Seadrift, TX

Fig. II-1. Locations of Plants Manufacturing Ethanolamines

D. REFERENCES*

1. "Chemical Profile on Ethanolamines," p. 9 in Chemical Marketing Reporter (Apr. 9, 1979).

2. J. L. Blackford, "Ethylene Oxide," pp. 654.5032R,S in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (September 1976).

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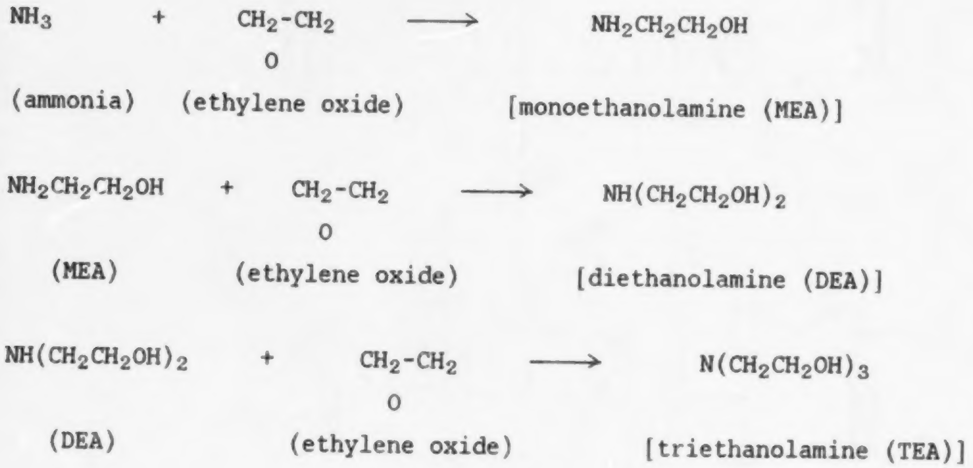
III. PROCESS DESCRIPTIONS

A. INTRODUCTION

Ethanolamines are produced commercially in the United States by the liquid-phase reaction of ethylene oxide and aqueous ammonia. Other methods of synthesizing ethanolamines have been developed, such as the reaction of ethylene chlorohydrin with ammonia or the hydrogenation of formaldehyde cyanohydrin; however, these methods are not commercially practiced.[1]

B. ETHANOLAMINES FROM ETHYLENE OXIDE AND AMMONIA

The ethanolamines are produced by the following series of chemical reactions:[1]



$$NH_3 + \underset{O}{CH_2-CH_2} \longrightarrow NH_2CH_2CH_2OH$$

(ammonia) (ethylene oxide) [monoethanolamine (MEA)]

$$NH_2CH_2CH_2OH + \underset{O}{CH_2-CH_2} \longrightarrow NH(CH_2CH_2OH)_2$$

(MEA) (ethylene oxide) [diethanolamine (DEA)]

$$NH(CH_2CH_2OH)_2 + \underset{O}{CH_2-CH_2} \longrightarrow N(CH_2CH_2OH)_3$$

(DEA) (ethylene oxide) [triethanolamine (TEA)]

The process is noncatalytic and is carried out in the liquid phase in the presence of water. The reactions are strongly exothermic, about 100 kJ per g-mole of ethylene oxide reacted.[2] The distribution of products that can be obtained is dependent on the ratio of ammonia to ethylene oxide used. Excess ammonia favors MEA formation. Also, desired product distribution can be achieved by recycling MEA and/or DEA to be further reacted with ethylene oxide.[1]

A typical flow diagram for the continuous manufacture of ethanolamines is shown by Fig. III-1. Ethylene oxide (stream 1) and aqueous ammonia (stream 2) are fed to a reactor. The reaction conditions usually are a temperature range of 50 to 100°C, a pressure of 1 to 2 MPa, and an excess of 28 to 50% aqueous ammonia.[1] The reactor effluent (stream 3) is stripped of unreacted ammonia and some water

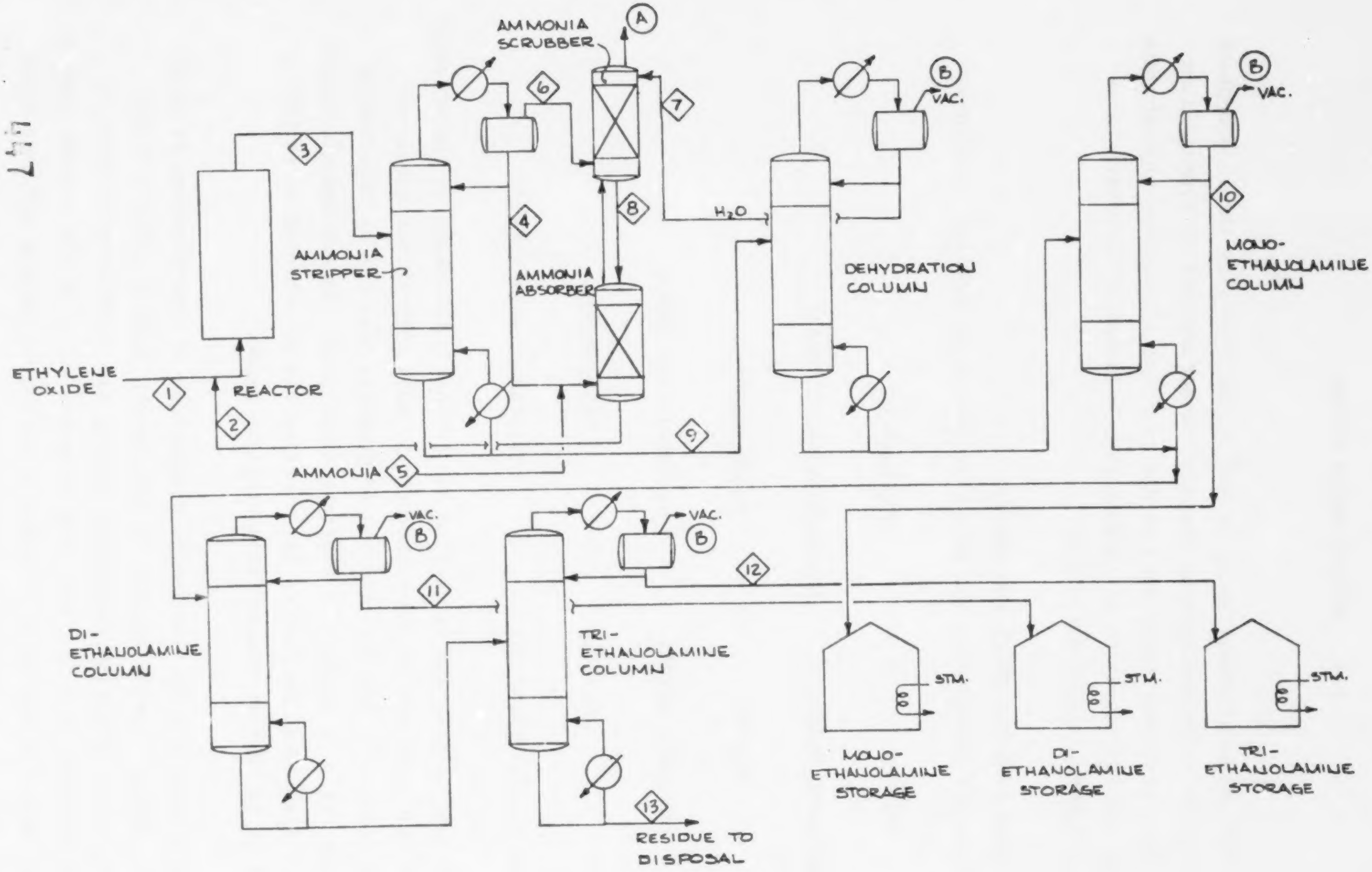


Fig. III-1. Production of Ethanolamines by the Ethylene Oxide—Ammonia Process

(stream 4) in an ammonia stripper operated under pressure. This ammonia, together with fresh feed (stream 5), is absorbed in recycled water in the ammonia absorber and fed back to the reactor (stream 2). The noncondensable overhead gas (stream 6) from the ammonia stripper is scrubbed of ammonia in an ammonia scrubber with recycle water (stream 7) and is vented (A). Inert gases enter the system with the ethylene oxide feed, which is stored under a nitrogen pressure pad.[3]

The ammonia stripper bottoms (stream 9) are vacuum distilled in a series of distillation columns to sequentially remove overhead water (stream 7), which is recycled, and MEA, DEA, and TEA (streams 10, 11, 12), which are products. Noncondensables from the vacuum distillation columns are vented (B) from the vacuum-jet discharges, and the vacuum-jet waste waters are discarded to waste treatment. The bottoms residue (stream 13) from the triethanolamine column is sent to waste treatment or is sold. The product storage tanks are ordinarily equipped with steam-heating coils to keep the products liquid and are padded with a dry inert gas such as nitrogen to prevent product discoloration.

C. PROCESS VARIATION

No detailed descriptive information appears to have been published on modern units for ethanolamines production. Various producers may be using widely different operating conditions and different distillation sequences.[2] It is not considered likely that these variations would have any appreciable effect on emission sources.

D. REFERENCES*

1. A. W. Hart, "Alkanolamines," pp. 810—814 in Kirk-Othmer Encyclopedia of Chemical Technology, 2d ed., vol. 1, edited by A. Standen *et al*., Wiley, New York, 1963.

2. H. W. Scheeline, "Ethylene Glycols, Glycol Ethers and Ethanolamines," Report No. 70, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (August 1971).

3. J. F. Lawson *et al*., IT Enviroscience, Inc., Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry——Ethylene Oxide Product Report (on file at EPA, ESED, Research Triangle Park, NC) (November 1978).

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IV. EMISSIONS

A. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

As indicated in Fig. III-1, there are two potential process emission sources. The ammonia scrubber vent (A) purges the small amount of nitrogen gas entering the system with the ethylene oxide feed, about 1 g per kg of ethanolamines.[1,2] There are no VOC emissions reported for this vent,[1—3] and the ammonia content is reported as approximately 100 ppm.[2] The vacuum distillation system vacuum-jet vents (B) purge the gases that may enter the system by leakage or that may be used for control. The overhead distillate products are either water or low-volatility, infinitely water-soluble organics; therefore the VOC emissions have been calculated to be at most only a trace.[1]

There are two waste streams that are potential secondary emission sources. One is the condensed steam from the vacuum jets. One producer reports this flow to be about 8 g per kg of ethanolamines and to contain 1% organics.[1] Such streams are sent to biological treatment.[1,2] The organics are low-volatility, infinitely water-soluble materials and as such should not have a significant potential for secondary emissions.[4] The other waste stream is the bottoms (stream 13, Fig. III-1) from the TEA column. One producer reports that this stream quantity is 22 g per kg of ethanolamines produced and that it is sold as a waste product.[1] Even if this material is disposed of by being burned or sent to landfill, its potential contribution to secondary emissions would be minor.

Fugitive and storage emissions are considered typical for the synthetic organic chemicals manufacturing industry and are not discussed in this abbreviated report. Fugitive and storage VOC emissions for the entire SOCMI are covered by separate EPA reports.[5,6]

B. REFERENCES*

1. Olin Chemicals, letter dated May 17, 1978, in response to EPA's request for information on emissions data on ethanolamines production facilities.

2. Dow Chemical U.S.A., letter dated Sept. 15, 1978, in response to EPA's request for information on emissions data on ethanolamines production facilities.

3. Jefferson Chemical Company, Inc., letter dated May 9, 1978, in response to EPA's request for information on emissions data on ethanolamines production facilities.

4. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions Report (on file at EPA, ESED, Research Triangle Park, NC) (October 1979).

5. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling Report (on file at EPA, ESED, Research Triangle Park, NC) (October 1978).

6. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emissions Report (on file at EPA, ESED, Research Triangle Park, NC) (March 1979).

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V. IMPACT ANALYSIS

A. INDUSTRY[1—3]

The ethanolamines industry does not contribute any significant process or secondary VOC emissions.

B. REFERENCES*

1. Olin Chemicals, letter dated May 17, 1978, in response to EPA's request for information on emissions data on ethanolamines production facilities.
2. Dow Chemical U.S.A., letter dated Sept. 15, 1978, in response to EPA's request for information on emissions data on ethanolamines production facilities.
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APPENDIX A

Table A-1. Physical Properties of Ethanolamines

Product	Monoethanolamine[a]	Diethanolamine[b]	Triethanolamine[c]
Synonyms	Ethanolamine, 2-aminoethanol, β-ethanolamine, colamine	DEA, di(2-hydroxyethyl)-amine, bis-hydroxyethylamine, diethylolamine, diolamine	2,2',2"-Trihydroxyethylamine
Molecular formula	C_2H_7NO	$C_4H_{11}NO_2$	$C_6H_{15}NO_3$
Molecular weight	61.08	105.14	149.19
Physical state	Liquid	Liquid-solid	Liquid-solid
Vapor pressure	800 Pa at 60°C (6 mm Hg)	667 Pa at 138°C (5 mm Hg)	<1.3 Pa at 20°C (0.01 mm Hg)
Boiling point	170°C at 101.3 kPa (760 mm Hg)	269.1°C at 101.3 kPa (760 mm Hg)	277°C at 20.0 kPa (150 mm Hg)
Melting point	10.3°C	28.0°C	21.2°C
Liquid specific gravity	1.0180 at 20°C/4°C	1.0919 at 30°C/20°C	1.1241 at 20°C/4°C
Water solubility	Infinite	Infinite	Infinite

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[a] J. Dorigan, B. Fuller, and R. Duffy, "Ethanolamine," p. AII-230 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals* *(Chemicals D-E)*, MTR-7248, Rev. 1, Appendix, Mitre Corp., McLean, VA (September 1976).

[b] *Ibid.*, "Diethanolamine," p. AII-74.

[c] *Ibid.*, "Triethanolamine" (Chemicals O-Z), p. AIV-260.

REPORT 8

ETHYLENE GLYCOL

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Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

November 1980

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D55E

CONTENTS OF REPORT 8

Page

I. ABBREVIATIONS AND CONVERSION FACTORS I-1

II. INDUSTRY DESCRIPTION II-1
- A. Reason for Selection II-1
- B. Ethylene Glycols Usage and Growth II-1
- C. Domestic Producers II-3
- D. References II-6

III. PROCESS DESCRIPTION III-1
- A. Introduction III-1
- B. Model Process——Ethylene Glycol from Ethylene Oxide III-2
- C. Other Processes III-6
- D. References III-8

IV. EMISSIONS IV-1
- A. Model Plant IV-1
- B. Sources and Emissions IV-1
- C. References IV-6

V. APPLICABLE CONTROL SYSTEMS V-1
- A. Types of Controlled Emissions V-1
- B. References V-4

VI. IMPACT ANALYSIS VI-1
- A. Environmental and Energy Impacts VI-1
- B. Control Cost Impact VI-3
- C. References VI-10

VII. SUMMARY VII-1

APPENDICES OF REPORT 8

A. PHYSICAL PROPERTIES OF GLYCOLS

B. AIR-DISPERSION PARAMETERS

C. LIST OF EPA INFORMATION SOURCES

D. FUGITIVE-EMISSION FACTORS

E. COST ESTIMATE SAMPLE CALCULATIONS

F. EXISTING PLANT CONSIDERATIONS

TABLES OF REPORT 8

Number		Page
II-1	Ethylene Glycol Usage and Growth	II-2
II-2	Ethylene Glycols Capacity as of 1980	II-4
IV-1	Uncontrolled Emissions from Ethylene Glycol Model Plant	IV-3
V-1	Controlled Emissions from Ethylene Glycol Model Plant	V-2
VI-1	Environmental Impact of Controlled Model Plant	VI-2
VI-2	Annual Cost Parameters	VI-4
VII-1	Emission Summary for Model Plant	VII-2
A-1	Properties of (Mono)-Ethylene Glycol	A-1
A-2	Properties of Diethylene Glycol	A-2
A-3	Properties of Triethylene Glycol	A-3
B-1	Air-Dispersion Parameters	B-1
F-1	Emission Controls Currently Used	F-2

FIGURES OF REPORT 8

Number		Page
II-1	Location of Plants Manufacturing Ethylene Glycol	II-5
III-1	Flow Diagram for Ethylene Glycol	III-3
III-2	Flow Diagram for Ethylene Glycol Process Variations	III-5
VI-1	Capital Cost vs Plant Capacity for Surface-Type Condensers	VI-6
VI-2	Annual Cost vs Plant Capacity for Surface-Type Condensers	VI-7
VI-3	Cost Effectiveness vs Plant Capacity for Surface-Type Condensers	VI-8

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Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
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68°F = 20°C

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PREFIXES

Prefix	Symbol	Multiplication Factor	Example
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G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Ethylene glycol was selected for study because preliminary estimates indicated that total emissions of volatile organic compounds (VOC) from its manufacture were high and because an increase in consumption was expected to continue.

The manufacture of (mono)-ethylene glycol (EG) from ethylene oxide results in production of diethylene glycol (DEG) and triethylene glycol (TEG) as principal co-products. These compounds are practically odorless, stable, colorless liquids, having greater densities and viscosities and higher boiling points than water.[1] Some physical properties of the ethylene glycols are given in Appendix A.

B. ETHYLENE GLYCOLS USAGE AND GROWTH

The 1980 production capacity of ethylene glycol in the United States was 2442 Gg/yr.[2,3] The 1979 production was 2066 Gg, or 85% of this capacity.[4] The estimated production capacity of diethylene glycol is 238.6 Gg/yr,[5] with the 1978 production being 168.8 Gg, or 71% of this capacity.[4] The triethylene glycol production capacity is estimated to be 82.6 Gg/yr,[6] with the 1978 production being 54.4 Gg, or 66% of this capacity.[4] Consumption during 1979—1984 is expected to increase at an average annual rate of 4% for ethylene glycol,[2] 4% for diethylene glycol,[5] and 2% for triethylene glycol.[6] If announced new plant constructions remain on schedule and no shortage of ethylene develops, the supply will be ample to meet projected demands through 1984.[2]

The uses of ethylene glycols and their expected growth rates are given in Table II-1.[2,5,6] Ethylene glycol, the most important of the glycols, was first commercially manufactured in 1925. Today its consumption rate makes it one of the more important of the synthetic organic chemicals. The largest use (approximately 43%) of ethylene glycol is for permanent-type antifreeze for liquid-cooled motor vehicles.

High-purity ethylene glycol is used to manufacture polyethylene terephthalate ester fibers and films. Approximately 40% of the ethylene glycol produced is used in polyester fiber production, and about 6% is used in polyester films and resins, the fastest growing use.[2]

Table II-1. Usage and Growth of Ethylene Glycols

End Use	1979 Use (%)	Average Growth for 1979—1984 (%/yr)
Ethylene Glycol[a]		
Antifreeze	43	2
Polyester fibers	40	4
Polyester film	3.5	9.4
Polyester bottles	2.5	16
Other[b]	11	4.5
Total	100	3.8
Diethylene Glycol[c]		
Unsaturated polyester resins, polyester polyols for polyurethanes	35	
Triethylene glycol	13	
Morpholine	8	
Natural-gas dehydration	7	
Textile agents	6	
Udex extraction solvent	6	
Dioxane	6	
Plasticizers and surfactants	19	
Exports		
Other[d]		
Total	100	4
Triethylene Glycol[e]		
Natural gas dehydration	34	
Vinyl plasticizer	16	
Solvent	15	
Humectant	14	
Unsaturated polyester resins, polyester polyols for polyurethanes	6	
Exports	15	
Other		
Total	100	2

[a] See ref 2.

[b] Other uses include asphalt-emulsion paints, heat-transfer agents, low-pressure laminates, brake fluids, glycol diacetate, low-freezing dynamite, solvents, extractants for various purposes, solvent mixutre for cellulose esters and ethers, cosmetics, lacquers, alkyd resins, printing inks, wood stains, adhesives, leather dyeing, textile processing, tobacco, and deicing fluid (see ref 2).

[c] See ref 5.

[d] Other uses include blending into antifreeze, plasticizer for cork adhesives, coupling agent for cosmetics and soaps, and as a humectant for tobacco (see ref 5).

[e] See ref 6.

Diethylene glycol is usually manufactured as a co-product of ethylene glycol production. Most diethylene glycol (35%) is used to manufacture polyurethane and unsaturated polyester resins. This market is expected to grow 8 to 9% annually.[5]

Triethylene glycol, also a co-product of ethylene glycol production, is used principally as a natural-gas dehydrant, which consumes 34% of the triethylene glycol manufactured. If natural-gas price ceilings are lifted and gas production increases, triethylene glycol consumption would be expected to increase. No new uses for triethylene glycol are foreseen.[6]

C. DOMESTIC PRODUCERS

Eleven producers were operating 14 ethylene glycol plants at the end of 1979.[2] Chemical Exchange Co. and Dixie Chemical Co. reportedly recover diethylene glycol and triethylene glycol from purchased glycol bottoms.[5,6] Table II-2 lists the producers, locations, and capacities for each of the principal glycol compounds produced. Figure II-1 shows the plant locations.

Ethylene glycol is manufactured principally by the noncatalytic hydration of ethylene oxide. Diethylene glycol and triethylene glycol are co-products of this process. All ethylene glycol manufacturers using the process also produce their own ethylene oxide feedstock.[1] Diethylene glycol may be produced by the reaction of ethylene glycol and ethylene oxide, but this is not done to any large extent. Approximately 15% of the triethylene consumed is produced by reacting diethylene glycol with ethylene oxide.[7]

In 1978 Oxirane began production of ethylene glycol with an acetoxylation process developed by Halcon International, Inc. With this process ethylene glycol is produced directly from ethylene with acetic acid in the presence of a catalyst to form mono- and diacetates. These compounds are further hydrolyzed to ethylene glycol. The plant operated intermittently during 1978 and 1979 and was shut down in November 1979 because of severe corrosion problems. Oxirane reportedly is exploring alternative uses for the plant but has given no time table for this evaluation.[2,8]

Table II-2. Ethylene Glycols Capacity as of 1980[a]

Company	Location	Production Capacity (Gg/yr) Ethylene Glycol[b]	Diethylene Glycol[c]	Triethlene Glycol[d]
BASF Wyandotte	Geismar, LA	113	15.9	
Calcasieu Chemical	Lake Charles, LA	82		
Celanese Chemical	Clear Lake City, TX	227	20.4	4.5
Chemical Exchange[e]	Houston, TX		NA	NA
Dixie Chemical[e]	Bayport, TX		NA	NA
Dow Chemical U.S.A.	Freeport, TX	116	34.0	22.7
	Plaquemine, LA	159		
Eastman Kodak	Longview, TX	82	8.2	0.5
Northern Natural Gas	Morris, IL	91	6.8	
Olin	Brandenburg, KY	18	NA	2.3
PPG Industries[f]	Beaumont, TX	82	8.2	0.5
Shell Chemical	Geismar, LA	154	11.3	11.3
Texaco	Port Neches, TX	150	36.3	6.8
Union Carbide[g]	Seadrift, TX	329	97.5	34.0
	Taft, LA	567		
	Penneulas, PR	272		
Total		2442[h]	238.6	82.6

[a] See refs 2, 5, and 6.

[b] Reported plant capacities vary from one reference to another. The total EG capacity reported by Chemical Marketing Reporter is 2982.4 Gg/yr; see ref 4.

[c] Some diethylene glycol capacities are based on 10% of ethylene glycol capacity and represent only the capability to produce.

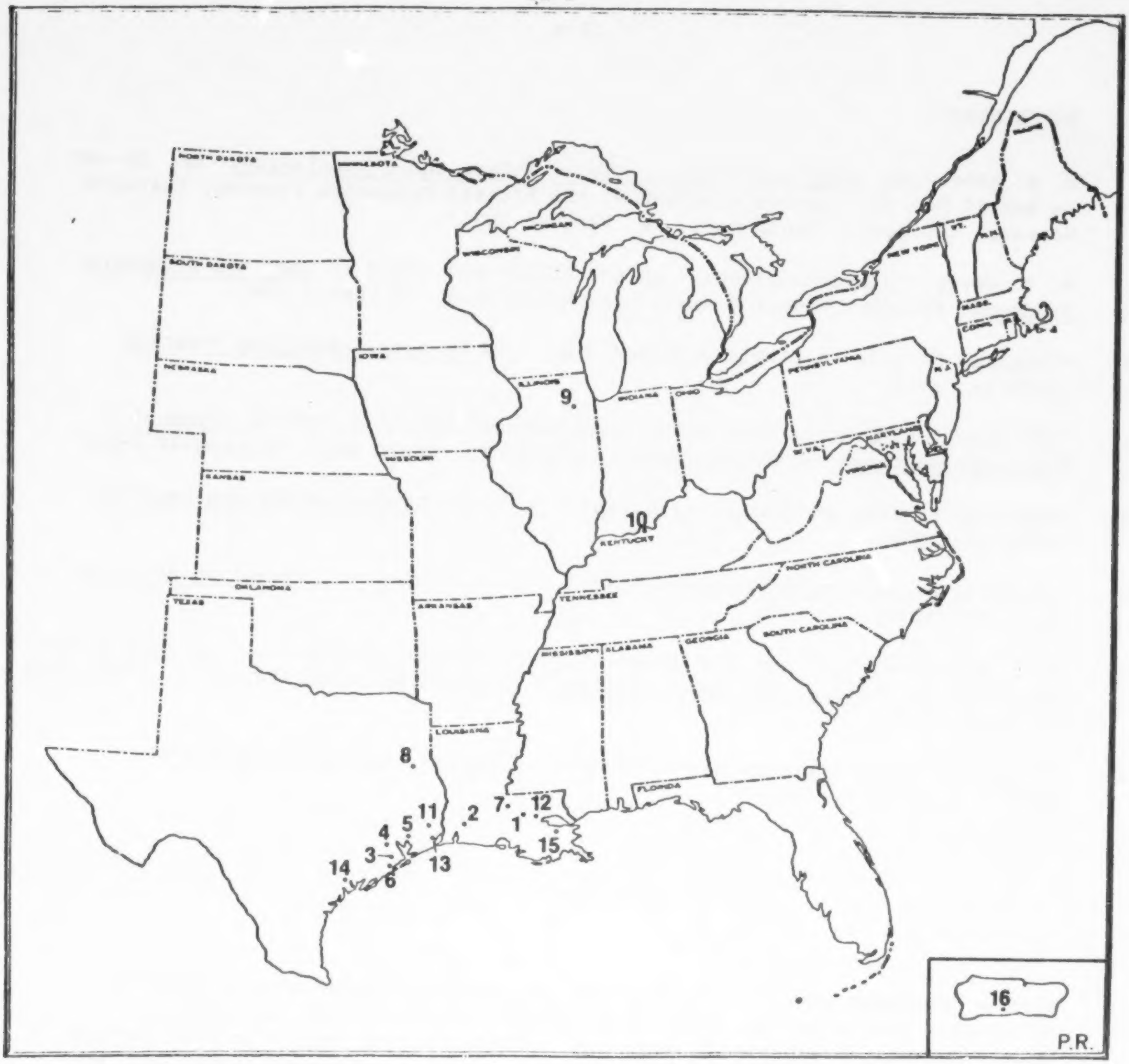
[d] Capacities to produce triethylene glycol are flexible.

[e] DEG and TEG are obtained by distilling glycol still bottoms purchased from other producers; see refs 5 and 6.

[f] PPG closed their Guayanilla, PR, plant in 1978 due to lack of ethylene; see ref 2.

[g] Union Carbide has announced plans to construct a 408-Gg/yr ethylene glycol facility at a site to be named later; see ref 2.

[h] ICI Americas, Inc. is building an ethylene oxide facility at Bayport, TX. Dow Chemical has announced another ethylene oxide facility with 1983 startup (no location specified). Both will produce some ethylene glycol; see ref 2.



1. BASF Wyandotte, Geismar, LA
2. Calcasieu, Lake Charles, LA
3. Celanese, Clear Lake City, TX
4. Chemical Exchange, Houston, TX
5. Dixie Chemical, Bayport, TX
6. Dow Chemical, Freeport, TX
7. Dow Chemical, Plaquemine, LA
8. Eastman Kodak, Longview, TX
9. Northern Natural Gas, Morris, IL
10. Olin, Brandenburg, KY
11. PPG, Beaumont, TX
12. Shell, Geismar, LA
13. Texaco, Port Neches, TX
14. Union Carbide, Seadrift, TX
15. Union Carbide, Taft, LA
16. Union Carbide, Penuelas, PR

Fig. II-1. Locations of Plants Manufacturing Ethylene Glycols

D. REFERENCES*

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2. R. T. Gerry, "Ethylene Glycol," pp 652.5030A—652.5030R in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1980).

3. "Chemical Profile on Ethylene Glycol," p. 9 in Chemical Marketing Reporter (July 24, 1978).

4. "CEH Manual of Current Indicators—Supplemental Data," p. 256 in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1980).

5. "Chemical Profile on Diethylene Glycol," p. 9 in Chemical Marketing Reporter (Nov. 12, 1979).

6. "Chemical Profile on Triethylene Glycol," p. 9 in Chemical Marketing Reporter (Aug. 13, 1979).

7. T. F. Killilea, "Di- and Triethylene Glycols Salient Statistics," pp. 652.5130A—652.5130F in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1978).

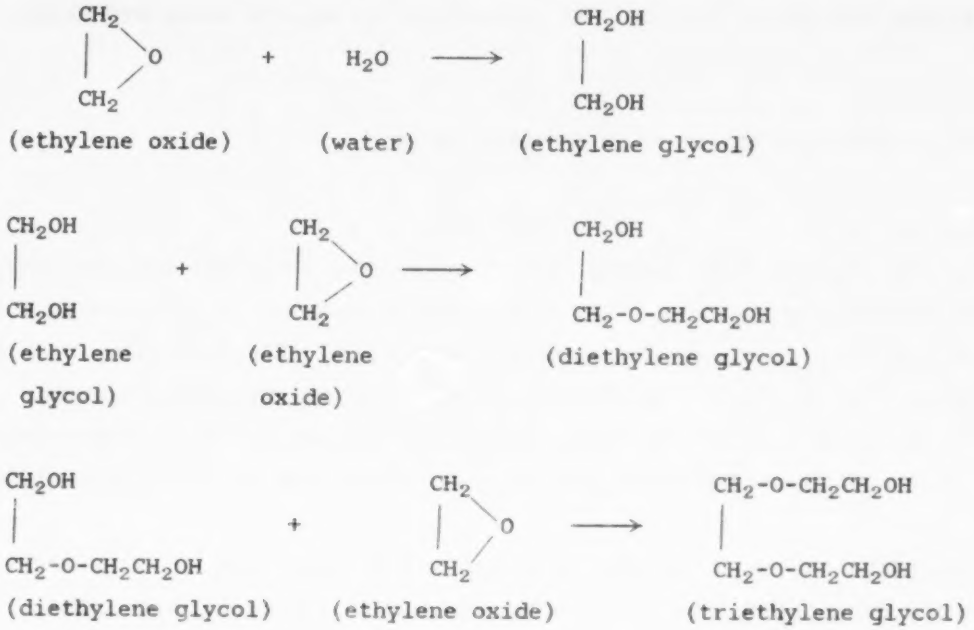
8. "Process Failure Squeezes Glycol Market," Chemical and Engineering News 57(49), 6 (Dec. 3, 1979).

*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Ethylene glycol, CH_2OHCH_2OH, is manufactured on a very large scale throughout the world by the addition of water to ethylene oxide (EO). The ethylene glycol (EG) formed will react with additional ethylene oxide to form diethylene glycol (DEG), triethylene glycol (TEG), and other higher homologs. The chemical equations are as follows:



The normal weight ratios of co-products formed are 87 to 88.5 wt % ethylene glycol, 9.3 to 10.5 wt % diethylene glycol, and 2.2 to 2.5 wt % triethylene glycol. These three products constitute an overall yield of 92.5 to 95.5% of theoretical, based on the ethylene oxide feed.[1]

In the United States the principal method of manufacture of ethylene glycol is by noncatalyzed pressure hydration of ethylene oxide.[2] In this process a residence time of 1 hr at 200°C and a pressure of 1380 kPa is common. Present-day practice is to use the noncatalyzed pressure hydration process because the alternative acid catalyst process results in problems with acid residue in the product.[1] In the acid hydration process ethylene oxide is converted to ethylene glycol by contact with a 0.5 to to 1.0% sulfuric acid catalyst solution at 50 to 70°C for 30 min.[3]

In both processes diethylene and triethylene glycols are formed as co-products. The greater the ratio of water to ethylene oxide in the feed, the greater will be the proportion of (mono)-ethylene glycol in the reactor product. The water:oxide weight ratios of the order of 8:1 are used. Ratios of the products formed to a limited extent can be varied to meet market demand by varying the feed ratio and/or other process variables.[1]

The Oxirane Corp. plant at Channelview, TX, which began production in 1978 but was shut down in 1979, produced ethylene glycol by the acetoxylation process. All major production facilities use the conventional ethylene oxide hydration process.

B. MODEL PROCESS——ETHYLENE GLYCOL FROM ETHYLENE OXIDE

1. Process Description

The process flow diagram shown in Fig. III-1 represents a typical noncatalyzed ethylene oxide hydration process. The continuous process is carried out in the liquid phase, and the reactions are strongly exothermic. Theoretically, 0.71 kg of EO is required to produce 1 kg of EG; 0.83 kg of EO is required to produce 1 kg of DEG; and 0.88 kg of EO is required to produce 1 kg of TEG.[1] The model* process produces an overall product and co-product yield of 94.8% of theoretical.

Refined liquid EO (stream 1), makeup water (stream 2), and recycle water are mixed under pressure (1380 kPa), preheated, and fed to the hydrolyzer. The feed solution (stream 3) contains approximately 8 kg of water per kg of EO. The reactor effluent, heated by the exothermic heat of hydration, exits (stream 4) the hydrolizer at 200°C and enters a multiple-effect evaporator system for removal of water.

A portion of the vapor from the first evaporator effect is purged (stream 5) to remove light impurities from the system. The remainder of the vapor and the vapors from the remaining evaporator effects are condensed and recycled (stream 6). The evaporator calandria and the condenser on the final evaporator effect are vented (A) to remove noncondensable gases.

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*See p I-2 for a discussion of model plants.

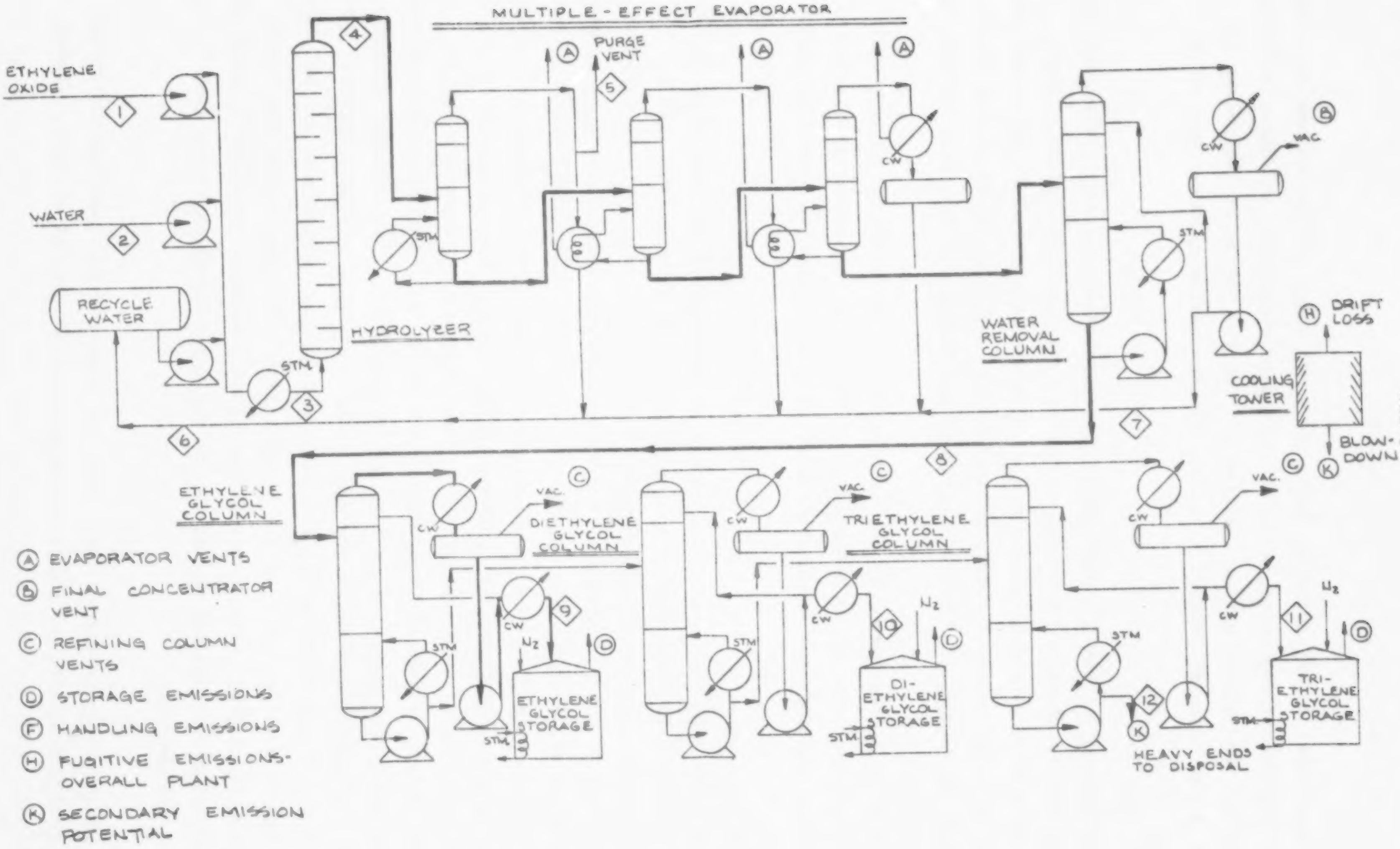


Fig. III-1. Flow Diagram for Uncontrolled Model Plant Producing Ethylene Glycol by Noncatalyzed Hydration of Ethylene Oxide

The concentrated glycol solution then enters the water removal column for final drying. The remaining water is vacuum distilled overhead, condensed, and recycled (stream 7). The glycol mixture (stream 8) from the bottom of the column is passed to the refining section. Vapors from the vacuum producer are vented (B).

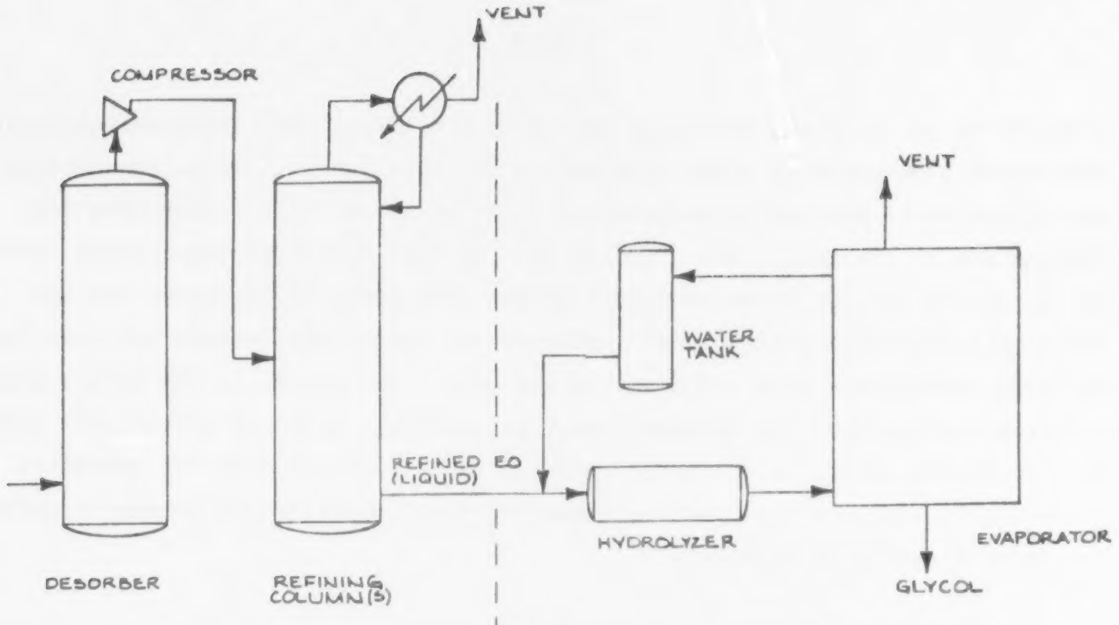
Ethylene glycol (stream 9), diethylene glycol (stream 10), and triethylene glycol (stream 11) are distilled overhead in separate vacuum distillation columns. Steam-jet ejectors used to maintain the vacuum on each distillation column are vented (C). The residual heavy ends discharged from the bottom of the final distillation column (stream 12) are stored for disposal or for sale as by-products.

A one month's storage capacity for each product is provided in conventional cone-roof tanks. The tanks are padded with nitrogen to prevent absorption of atmospheric moisture and are heated in the winter to prevent excessive viscosity.

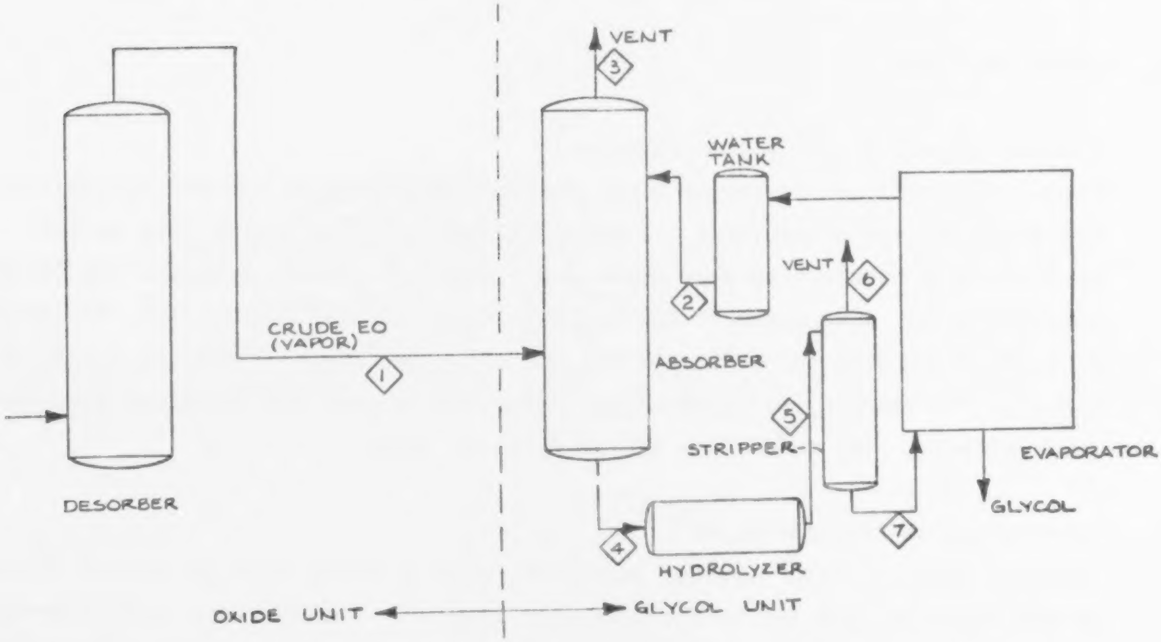
2. Process Variations

There are existing ethylene glycol plants in which crude EO vapor from the EO plant desorber[4] is fed directly to the EG plant[5] as shown in Fig. III-2. The crude EO vapor (stream 1) is reabsorbed into water (stream 2) by an absorber that is part of the glycol unit. The unabsorbed vent gases (stream 3) accompanying the crude EO are vented. The EO solution (stream 4) then enters the hydrolizer. The effluent (stream 5) from the hydrolizer is passed to a stripper, where the remaining gases and light hydrocarbons (stream 6) are separated and vented. The degassed glycol solution (stream 7) then enters the evaporator system. Thus the emissions normally associated with EO refining operations are carried over to the glycol plant, where they are discharged.[5] The combined emissions in both cases are essentially the same. The heavy ends (largely glycols) normally separated in the EO refining operations are likewise carried over to the glycol plant and ultimately end up in the product or are discharged with the heavy ends from the glycol refining operation. Thus secondary emissions associated with glycol production may be increased, while secondary emissions from EO production may decrease.

Large amounts of high-temperature steam are required for removing the excess water required by the hydrolysis reaction in production of glycols. Common



CONVENTIONAL PROCESS: REFINED OXIDE FED TO GLYCOL UNIT



VARIATION PROCESS: CRUDE OXIDE FED TO GLYCOL UNIT

Fig. III-2. Process Variations for Producing Ethylene Glycol by Noncatalyzed Hydration of Ethylene Oxide

practice is to integrate the oxide unit with the glycol unit on an energy basis. The excess high-pressure steam produced in the oxide unit is often consumed by the glycol unit, and low-pressure steam from the glycol unit is returned for consumption in the oxide unit. Similarly, the heat from high-temperature sources in the glycol unit is often recovered by the feed water to the oxide reactor steam generators being preheated.[5] Schemes for energy utilization and conservation may vary extensively from one plant to the next. New plants in the future might be sized and designed for maximum energy utilization, with the glycol unit sized for the amount of energy available from the oxide unit and with the operating temperatures and pressures for the evaporators and distillation columns selected for optimum energy availability.[1,5]

Many variations in the design and operation of the water removal section of the plant exist between existing plants. Also, the number of product distillation steps or columns used by different plants may vary. Some plants do not recover diethylene glycol or heavier glycols but instead sell the still bottoms to independent producers for recovery of the heavier glycol by-products.

C. OTHER PROCESSES

1. Ethylene Glycol Directly from Ethylene

Halcon International developed a new acetoxylation process for making ethylene glycol directly from ethylene. Ethylene is reacted with acetic acid in the presence of a catalyst to form mono- and diacetates. These products are further oxidized to ethylene glycol. The Oxirane Corp. plant at Channelview, TX, which went on-stream June 16, 1978, but was shut down in November 1979, is the first plant built based on this technology. Specific process and emissions data are not available. The future use of the plant is uncertain.[6,7]

2. Carbonation of Ethylene Oxide

Ethylene oxide, carbon dioxide, and water (with a sodium bromide—sodium bicarbonate catalyst) are fed to a carbonation reactor. The ethylene carbonate that is formed is then hydrolyzed to glycols in the same reactor system. The amount of water required by this process is much lower than that required by the conventional process. The process yields 98% ethylene glycol. The overall production cost is estimated to be slightly lower than that for conventional hydration since the cost of removing water is considerably less. However, the corrosiveness of the catalyst solution requires that special materials of construction be used for the plant. The process has not been commercialized.[1]

3. Ethylene Glycol from Formaldehyde, Carbon Monoxide, and Water
From 1940 to 1969 Du Pont produced ethylene glycol by the reaction of formaldehyde, carbon monoxide, and water, followed by hydrogen reduction of the intermediate glycolic acid to obtain the ethylene glycol. Du Pont shut down the plant because of pollution problems. PPG is reportedly studying a modification of the process and Chevron Research recently applied for patents using a hydrogen fluoride catalyst rather than the sulfuric acid catalyst used by Du Pont.[1,8,9]

4. Ethylene Glycol from Hydrogenation and Hydrogenolysis of Carbohydrate
In the early 1970s[3] ICI United States, Inc., produced ethylene glycol by fermentation of molasses. The plant is now on standby.[8]

5. Ethylene Glycol from Synthesis Gas
Union Carbide Corporation is reportedly developing a process for producing ethylene glycol from synthesis gas.[8]

D. REFERENCES*

1. H. W. Scheeline, Ethylene Glycols, Glycol Ethers, and Ethanolamines, pp. 10—49 in Report 70, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (August 1971).
2. P. H. Miller, "Glycols," p. 642 in Kirk-Othmer Encyclopedia of Chemical Technology, 2d ed., vol. 10, edited by A. Standen *et al.*, Interscience, New York, 1966.
3. F. A. Lowenheim and M. K. Moran, "Glycols," pp. 397—402 in Faith, Keys, and Clark's Industrial Chemicals, 4th ed., Wiley-Interscience, New York, 1975.
4. See Fig. III-1 in J. F. Lawson and V. Kalcevic, IT Enviroscience, Inc., Ethylene Oxide (in preparation for EPA, ESED, Research Triangle Park, NC).
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IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemical have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. MODEL PLANT*

The model plant for this study has a total glycol (EG, DEG, and TEG) capacity of 170 Gg/yr based on 8760 hr of operation annually.** The capacity of existing production units based on the EO hydration process varies from 15 to about 325 Gg/yr. The recent trend in the industry has been to construct large-capacity units or to expand the capacity of existing units.

The model plant utilizes the model noncatalyzed ethylene oxide hydration process described in Sect. III-B. Although not an actual operating plant, it is typical of existing plants utilizing the noncatalyzed ethylene oxide hydration process.

Storage tanks for the model plant were sized to provide 1 month of storage capacity for each product. Characteristics of the model plant that are important in air-dispersion modeling are given in Appendix B.

B. SOURCES AND EMISSIONS

The process emissions estimated for the ethylene glycol model plant are based on information given in a trip report of a visit to Union Carbide[1] and in responses to EPA's requests for information from selected companies (see Appendix C), together with data from a report published by Stanford Research Institute[2] and an understanding of the process chemistry and yields. The storage and handling emissions were calculated based on physical properties. The fugitive emissions due to leaks are based on the data referenced in Appendix D. Uncontrolled air emission data reported by individual plants producing ethylene glycol vary widely from plant to plant. These differences appear to be related largely to differences in plant design and operation and in how the reported air emissions were determined.

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculatons, the error introduced by assuming continuous operation is negligible.

The glycols are water soluble, have low vapor pressures, and boil at higher temperatures than water. Thus glycol emissions tend to be small. The principal volatile impurities in the reactor product are ethylene oxide and acetaldehyde. Both these compounds are infinitely soluble in water and tend to reabsorb in the condensate from the evaporators or distillation column vents. The quantity of air emissions is related to the manner in which these streams are handled. Those plants that vent the evaporator purge stream and the distillation column steam-jet ejectors directly to atmosphere as vapor have large emissions. If barometric-type condensers are used to condense and absorb these discharges, the process emissions are reduced, but the fugitive emissions from the cooling tower and the secondary emissions from treatment of cooling tower blow-down water may become significant. If surface-type condensers are used and the condensate is isolated from the cooling water, the cooling tower emissions are eliminated. However, the secondary emissions from treatment and disposal of the condensate are increased.

The model-plant uncontrolled emission rates given in Table IV-1 were calculated based on the model-plant characteristics and operating and emission data from existing plants. The model-plant overall product and by-product yield is 94.8%, with an EO conversion factor of 99%. Heavies discharged from the bottom of the triethylene glycol column account for 2.5% of the losses. Air emission and the purge stream and cooling tower blow-down losses make up the remaining 2.7%.

1. Process Emissions

Uncontrolled process emissions from the model plant originate from the evaporator first-effect purge stream (stream 5, Fig. III-1), the evaporator calandria vents

Table IV-1. Total VOC from Uncontrolled Emissions from Production of Ethylene Glycol in a Model Plant

Emission Source	Stream Designation (Fig.III-1)	Emissions Ratio[a] (g/kg)	Emissions Rate[b] (kg/hr)
Process emissions[c]	5,A,B,C	0.0595	1.16
Storage emissions[d]	D	0.0028	0.05
Handling emissions	F	0.0010	0.02
Fugitive emissions[e]	H	4.7407	92.05
Secondary emissions[f]	K	0.3542	6.88
Total		5.1582	100.16

[a] g of emission per kg of total products produced.

[b] For the 170-Gg/yr model plant based on an average glycol production rate of 19,417 kg/hr.

[c] Due to direct emissions from evaporator calandria vent (A). Emissions from other process vents (vent B, water removal column vacuum ejector; vent C, glycol purification column vacuum ejectors; and stream 5, evaporator purge) are absorbed by the cooling water through use of barometric-type condensers and thus contribute to fugitive and secondary emissions.

[d] Principally from storage of ethylene glycol; emissions from storage of heavier glycols are negligible.

[e] Estimated sources of fugitive emissions are cooling water (4.6705 g/kg) and leakage from pumps and valves (0.0702 g/kg); contributors to cooling water fugitive emissions are stream 5 (4.6653 g/kg), vent C (0.0052 g/kg), and vent B (negligible).

[f] Secondary emissions result from treatment of cooling water blowdown; estimated contributors to cooling water secondary emissions are stream 5 (0.3534 g/kg), vent C (0.0007 g/kg), and vent B (negligible).

(A), the discharge from the water removal column steam-jet ejector (vent B), and the discharges from the distillation column ejectors (vents C).

The uncontrolled model plant incorporates barometric-type contact condensers to condense and absorb the vapor from the evaporator purge (stream 5) and the discharge from the various steam-jet ejectors (vents B and C). The emissions from these sources then circulate with the cooling water. Partial desorption occurs as the cooling water passes through the cooling water circuit and cooling tower. The remainder of the contaminants end up in the cooling tower blow-down stream. The evaporator calandria emissions for the uncontrolled model plant are vented directly to the atmosphere.

2. Storage Emissions

Due to their hygroscopic properties glycols are normally stored in tanks blanketed with nitrogen. The tanks are heated to prevent excessive viscosity in cold weather. Breathing losses are negligible because the tank temperature is controlled. Because of the low vapor pressure of glycols the emissions due to working losses are small for ethylene glycol and are negligible for the heavier glycols when calculated by the emission equations from AP-42[3] (see Table IV-1).

3. Handling Emissions

Emissions from loading of shipping vessels were calculated with the equations from AP-42.[4] Because of the low vapor pressure of the glycols the handling emissions are small (see Table IV-1).

4. Fugitive Emissions

Process pumps and valves that handle organic compounds under pressure are potential sources of fugitive emissions. The model plant is estimated to have 7 pumps, 38 process valves, and 3 relief valves handling light organics in the feed and water removal sections and 6 pumps and 15 valves in sections handling heavy organics under positive pressure. The fugitive-emission factors from Appendix D were applied to determine the fugitive emissions shown in Table IV-1.

The largest source of fugitive emissions is from the cooling tower. Partial desorption of organics contained in the cooling water occurs as the water passes through the cooling tower. The cooling water system emissions given in Table IV-1 are based on average desorption data reported by plants using barometric condensers.[5,6]

5. Secondary Emissions

Secondary VOC emissions can result from the handling and disposal of process waste liquid streams. The potential sources (source K) that exist for the model plant are the blow-down water from the cooling tower and from disposal of the heavy ends (stream 12). Due to the low volatility of the heavy ends stream the secondary emissions calculated for this stream were negligible. Secondary emissions from treatment of the cooling tower blow-down water are shown in Table IV-1. The calculations were based on wastewater treatment by a primary clarifier followed by an activated-sludge system and were done by the methods described in another EPA report on secondary emissions.[7]

C. REFERENCES*

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5. Shell Oil Co., letter dated Jan. 11, 1979, in response to EPA's request for information on emissions data on ethylene glycol production facilities.

6. BASF Wyandotte Corp., letter dated Nov. 27, 1978, in response to EPA's request for information on emissions data on ethylene glycol production facilities.

7. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

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V. APPLICABLE CONTROL SYSTEMS

A. TYPES OF CONTROLLED EMISSIONS

1. Process and Process-Related Emissions

Process emissions from the uncontrolled model plant are the result of direct atmospheric discharge from the vents (A) on the multiple-effect evaporator and from desorption of organics contained in the cooling water. Contamination of the cooling water results from its direct contact with the discharges from the steam-jet ejectors associated with the distillation column vents (B and C) and with the discharge from the evaporator purge stream (5) through use of barometric-type contact condensers on these streams.

To prevent the cooling water from becoming contaminated, the controlled model plant uses surface-type condensers to replace the barometric-type condensers. The condensate from the condenser is discharged to wastewater treatment. Uncondensed gases are vented to the atmosphere. A surface-type condenser is also used to control emissions from the evaporator vents (A) in the controlled model plant.

The installation of surface-type condensers to isolate the condensate from the cooling water eliminates fugitive emissions from the cooling tower. However, the condensate added to the wastewater increases secondary emissions. Also, the uncondensed gases vented from the surface condensers contain some VOC. The net reduction in emissions originating from all process sources (vents A, B, and C and stream 5) by application of surface condensers is 85%,* as indicated in Table V-1. This includes the overall change in direct process emissions plus the change in fugitive and secondary emissions related to process sources.

2. Storage and Handling Emissions

Emissions due to storage and handling of glycols remain uncontrolled in the model plant. Emissions from these sources are slight due to the low vapor pressure

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*This number was calculated by subtracting the controlled emissions originating from all process sources (0.0062 + 0.7720 = 0.7782 g/kg) from the uncontrolled emissions originating with streams 5, A, B, and C (0.0595 + 4.6705 + 0.3534 + 0.0007 + neg = 5.0842 g/kg) (see Table IV-1) to determine the net reduction in VOC emissions (5.0842 - 0.7782 = 4.306 g/kg) due to use of surface condensers instead of barometric condensers. The value 4.306 g/kg is 85% of 5.0842 g/kg.

Table V-1. Total Controlled VOC Emissions for Model-Plant Ethylene Glycol Production

Source	Stream Designation (Fig.III-1)	Control Device or Technique	Emission Reduction (%)	Emissions Ratio[a] (g/kg)	Emissions Rate[b] (kg/hr)
Process emissions[c]	5,A,B,C	Surface Condensers	85	0.0062	0.12
Storage emissions	D	None		0.0028	0.05
Handling emissions	F	None		0.0010	0.02
Fugitive emissions[d]	H	Inspection and Maintain	66	0.0240	0.47
Secondary emissions[e]	K	None		0.7720	14.99
Total			84 (Av)	0.8060	15.65

[a] g of emission per kg of total products produced.

[b] For the 170-Gg/yr model plant based on an average glycol production rate of 19,417 kg/hr.

[c] The net reduction in emissions originating from all process sources (vents A, B, and C and stream 5) is 85%; this includes overall change in direct process emissions plus change in fugitive and secondary emission related to process sources.

[d] The reduction in fugitive emissions applies to leakage from pumps and valves, which are reduced 66% by inspection and maintenance. Installation of surface condensers eliminated cooling tower fugitive emissions.

[e] Secondary emissions have increased due to condensate from vent condensers being added to wastewater.

of the product stored and the nitrogen-blanketed controlled-temperature storage techniques employed. Control options for storage and handling emissions are discussed in another EPA document.[1]

3. Fugitive Emissions

The principal fugitive emissions from the uncontrolled model plant are from desorption of volatile organics contained in the cooling water as it passes through the cooling tower. The source of cooling water contamination was eliminated in the controlled model plant by replacement of the contact condensers used in the uncontrolled model plant with surface-type condensers.

The remaining fugitive emissions result from leaks from pumps and valves even though much of the equipment is operated under vacuum. Emissions from pumps and valves can be controlled by an appropriate leak-detection system and repair and maintenance program. Controlled fugitive emissions calculated with the factors given in Appendix D are included in Table V-1; these factors are based on the assumption that major leaks are detected and corrected. Control measures for control of fugitive emissions are discussed in another EPA report.[2]

4. Secondary Emissions

The principal secondary emissions from the controlled model plant result from desorption of volatile organic compounds contained in the condensate from the vent condensers. The secondary emission data given in Table V-1 were calculated based on the characteristics and the estimated concentration of the volatile components in the condensate. Treatment by a conventional clarifier and activated-sludge system was assumed. No control system has been identified for the secondary emissions from wastewater treatment. Secondary emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry are discussed in another EPA report.[3]

B. REFERENCES*

1. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

2. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

3. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

1. Emission Reduction

An overall emission reduction of 84%, or 740.31 Mg/yr, is achieved (see Table VI-1) by application of the control systems described in Sect. V to the model plant described in Sects. III and IV.

The principal source of emissions from the uncontrolled model plant are fugitive emissions from the cooling tower. Contamination of the cooling water results from the use of contact condensers (barometric-type) on the process vents. The source of VOC contamination in the cooling water is eliminated by replacing the contact condensers with surface condensers. The condensate collected is discharged to the wastewater treatment system.

The cooling water required for both types of condensers is essentially the same. However, the exhaust from the evaporator calandria vents (A) is not condensed in the uncontrolled model plant. It is estimated that the amount of additional cooling water required for this condenser would be 152 liters/min.

It is possible that additional heat could be recovered in condensing the evaporator purge stream or the vapor from evaporator calandria vents through use of additional heat exchangers. The low-pressure steam generated might be used for the vacuum distillation operations or for operations in the EO plant. Because the potential exists for some producers to have excess steam on-site, it may not be practical for all producers to utilize heat recovery. No credit for heat recovery is taken for the controlled model plant.

2. 1979 Industry Emissions

The total VOC emissions from the domestic ethylene glycol industry in 1979 are estimated to be 6300 Mg, including the estimated emissions from process, fugitive, secondary, storage, and handling sources. The estimate is based on the 1979 level of total glycol production of 2066 Gg by the hydration of ethylene oxide process. To the extent available, actual emission data reported by the

Table VI-1. Environmental Impact of Controlled Ethylene Glycol Model Plant

Emission Source	Vent Designation (Fig.III-1)	Control Device or Technique	VOC Emission Reduction[a] (%)	VOC Emission Reduction[a] (Mg/yr)
Process emissions[b]	5,A,B,C	Surface condensers		9.11
Storage emissions	D	None		0
Handling emissions	F	None		0
Fugitive emissions[c]	H	Installation of surface condensers and detection and correction of major leaks		802.24
Secondary emissions[d]	K	None		-71.04
Total			84 (Av)	740.31

[a] For the 170-Gg/yr model plant based on full-capacity operation.

[b] Direct process emissions only are given here; secondary and fugitive emissions related to process discharges are given under those categories.

[c] Fugitive emissions are reduced 794.44 Mg/yr by replacing barometric condensers on process vents with surface condensers; correcting leaks in pumps and valves provides an additional 7.80-Mg/yr reduction.

[d] Secondary emissions increase 217.9%, or by 71.04 Mg/yr, due to the VOC in the condensate that is discharged to the wastewater treatment system.

individual plants were used to calculate the emissions (see Appendix C). For those plants where emission data were not available or where gaps appeared in reported data, the emissions were assumed to be the average of the reported emission for each emission source category. Fugitive emissions due to leaks were assumed to be controlled in 50% of the equipment.

B. CONTROL COST IMPACT

Estimated costs and cost-effectiveness data for control of VOC emissions resulting from the production of ethylene glycol are given in this section. Details of the model plant (Fig. III-1) are given in Sects. III and IV. Cost estimate sample calculations are included in Appendix E.

Capital cost estimates represent the total investment required for purchase and installation of all equipment and material needed for a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the costs of production lost during installation or startup, of research and development, or of land acquisition. If the control systems were retrofitted in an existing plant, difficulty may be experienced in finding space to accommodate the retrofitted control equipment in the existing plant layout. Because of these associated costs the cost of retrofitting emission control systems in existing plants may be appreciably greater than the cost for a new installation.

Bases for the annual cost estimates for the control alternatives include utilities, operating labor, maintenance supplies and labor, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors used are itemized in Table VI-2.

1. Process and Process-Related Emissions

Model-plant process emissions are controlled by surface-type condensers installed on each process vent. Separate condensers are required on the following: the evaporator purge (stream 5), the evaporator calandria vents (A), the water removal column (vent B), the ethylene glycol column (vent C), the diethylene glycol column (vent C), and the triethylene glycol column (vent C). The uncontrolled model plant has barometric (contact) condensers on all vents except the evaporator calandria vents (A). For a new plant the difference in installed costs for

Table VI-2. Annual Cost Parameters

Operating factor	8760 hr/yr[a]
Operating labor	$15/man-hr
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital cost
Capital recovery, 18%[b]	
Taxes, insurances, administration charges, 5%	
Utilities	
Cooling water	$\$0.026/m^3$ ($0.10/1000 gal)
Wastewater treatment (greater than 2 million gal/day)	$\$0.07/m^3$ plus $0.22/kg BOD ($0.25/1000 gal plus $0.10/lb BOD)

[a] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[b] Based on 10-year life and 12% interest.

surface condensers versus barometric condensers is primarily the difference in purchase costs of each type of condenser. Although the purchase cost of a surface condenser will be more than that of a barometric condenser, the difference is small in comparison to the total installed capital cost and is considered to be negligible for the purposes of this report.

The total estimated cost for the surface condenser on the evaporator calandria vents (A) is $50,000, which includes the cost of the equipment and of installing the equipment, piping, and insulation (see Appendix E for sample calculations). Figure VI-1 was plotted to show the variation of installed cost with plant capacity.

The condensers for the model plant are estimated to have a net annual cost of $350,000, which includes capital recovery, miscellaneous capital, maintenance, and utilities. The estimated variation of net annual cost with plant capacity is shown by Fig. VI-2.

The cost effectiveness of installing and operating emission controls for the model plant is $480 per Mg of VOC emissions removed. A plot of the estimated cost effectiveness versus plant capacity is shown by Fig. VI-3.

2. Storage and Handling

Storage and handling controls are not included in the controlled model plant since the rate of emissions from these sources is low. Control options for storage and handling emissions are covered in a recent EPA document.[1]

3. Fugitive Emissions

The principal fugitive emission source was eliminated by preventing the process cooling water from becoming contaminated through installation of surface condensers on the process vents. These controls are described under "Process and Process-Related Emissions."

Fugitive emissions due to leaks in pump and valve seals are controlled in the model plant by a program of inspection and maintenance. A recent EPA document describes fugitive emissions and their control measures.[2]

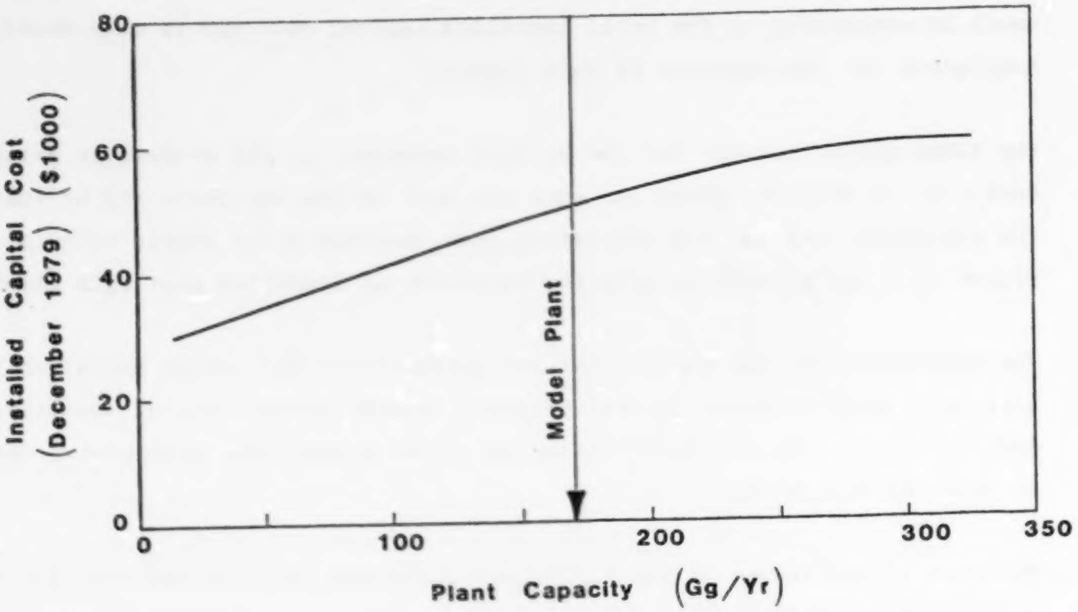

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Emission Control by Installation of Surface-Type Condensers

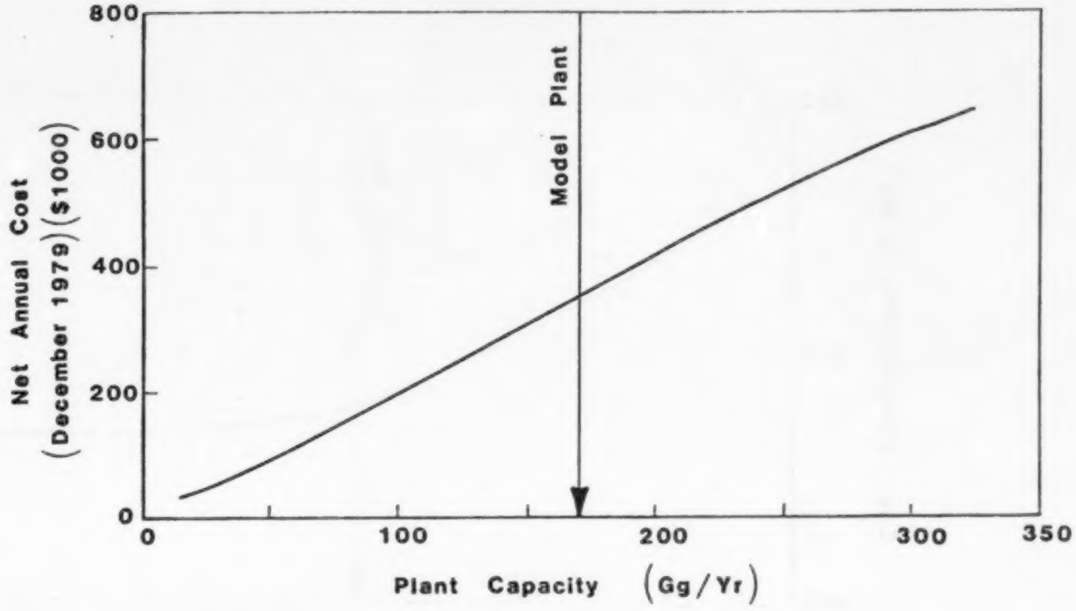

Fig. VI-2. Net Annual Cost vs Plant Capacity for Emission Control by Installation of Surface-Type Condensers

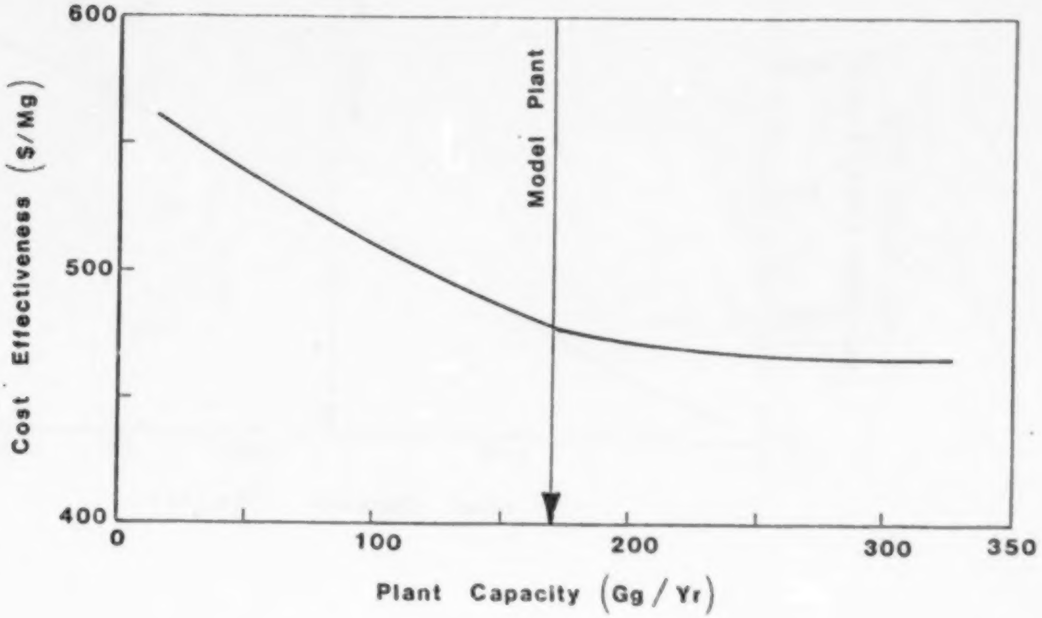

Fig. VI-3. Cost Effectiveness vs Plant Capacity for Emission Control by Installation of Surface-Type Condensers

4. Secondary Emissions

Control options for control of secondary emissions are covered in a recent EPA document.[3] No control system has been identified for the secondary emissions from the model plant.

C. REFERENCES*

1. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

2. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

3. J. J. Cudahy, IT Enviroscience, Inc., Secondary Emissions (September 1980) EPA/ESED report, Research Triangle Park, NC).

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VII. SUMMARY

Ethylene glycol is manufactured principally by the noncatalytic hydration of ethylene oxide,[1] with diethylene glycol and triethylene glycol produced as co-products. The domestic production capacity of ethylene glycol for 1980 was 2442 Gg,[2] with an industry utilization of approximately 85% of this capacity. The manufacture of antifreeze consumes about 43% of the ethylene glycol produced, and 46% is used to manufacture polyester fibers and films. The estimated consumption annual growth rate is 4%.[3]

Emission sources and uncontrolled and controlled emission rates for the ethylene glycol model plant are given in Table VII-1. The major emission source from the uncontrolled model plant is the fugitive emissions from the cooling tower. The contamination in the cooling water results from use of contact condensers on the process vents. The emissions are controlled by installing surface condensers, with the condensate collected and discharged to a wastewater treatment plant.

The emissions from storage and handling of glycols are slight and controls are normally not applied. Fugitive emissions due to leaks in pumps and valves are controlled by a program of inspection and maintenance. Secondary emissions become the major potential source of emissions after installation of surface condensers to control emissions from process-related sources. Control of secondary emissions is described in a recent EPA document.[4]

The total ethylene glycol industry VOC emissions are estimated to be 6300 Mg in 1979, with most of the uncontrolled VOC emissions coming from fugitive and secondary sources.

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[1] P. H. Miller, "Glycols," p. 642 in Kirk-Othmer Encyclopedia of Chemical Technology, 2d ed., vol. 10, edited by A. Standen et al., Interscience, New York, 1966.

[2] R. T. Gerry, "Ethylene Glycol," pp 652.5030A—652.5030R in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1980).

[3] "CEH Manual of Current Indicators——Supplemental Data," p. 256 in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1980).

[4] J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

Table VII-1. Emission Summary for Ethylene Glycol Model Plant[a]

Emission Source	Stream Designation (Fig.III-1)	VOC Emission Rate (kg/hr)	
		Uncontrolled	Controlled
Process emissions[b]	5,A,B,C	1.16	0.12
Storage emissions[c]	D	0.05	0.05
Handling emissions[c]	F	0.02	0.02
Fugitive emissions[d]	H	92.05	0.47
Secondary emissions[c,e]	K	6.88	14.99
Total		100.16	15.65

[a] For the 170-Gg/yr model plant based on an average glycol production rate of 19,417 kg/hr.

[b] Data apply to direct process emissions only.

[c] Storage, handling, and secondary emissions remain uncontrolled in the controlled model plant.

[d] Principal source of fugitive emissions in the uncontrolled model plant is the process cooling water; cooling water contamination is eliminated by the contact condensers on the process vents being replaced with surface-type condensers.

[e] Secondary emission increase in the controlled model plant due to condensate from the vent condensers being added to the wastewater.

APPENDIX A

Table A-1. Properties of (Mono)-Ethylene Glycol*

Synonyms	Glycol, ethandiol-1,2
Molecular formula	$C_2H_6O_2$
Molecular weight	62.1
Physical state	Liquid
Density	1.110 g/ml at 25°C
Vapor pressure	16 Pa at 25°C
Boiling point	197.3°C
Water solubility	Infinite

*From: Properties and Uses of Glycols, Dow Chemical USA, Midland, MI, 1961.

Table A-2. Properties of Diethylene Glycol*

Synonyms	Glycol ether
Molecular formula	$C_4H_{10}O_3$
Molecular weight	106.1
Physical state	Liquid
Density	1.113 g/ml at 25°C
Vapor pressure	1.3 Pa at 25°C
Boiling point	244.8°C
Water solubility	Infinite

*From: Properties and Uses of Glycols, Dow Chemical USA, Midland, MI, 1961.

Table A-3. Properties of Triethylene Glycol*

Synonyms	
Molecular formula	$C_6H_{14}O_4$
Molecular weight	150.2
Physical state	Liquid
Density	1.119 g/ml at 25°C
Vapor pressure	<1.3 Pa at 25°C
Boiling point	288°C
Water solubility	Infinite

*From: *Properties and Uses of Glycols*, Dow Chemical USA, Midland, MI, 1961.

APPENDIX B

Table B-1. Air-Dispersion Parameters for Model Plant with a Capacity of 170 Gg/yr

Source	Total VOC Emissions Rate[a] (g/sec)	Vent Height[b] (m)	Vent Diameter[b] (m)	Discharge Temperature[b] (K)	Flow Rate[b] (m^3/sec)	Discharge Velocity[b] (m/sec)
			Uncontrolled Emissions			
Process emissions for evaporator calandria (3 vents)	0.321	12.2	0.05	373	0.033	17
Storage emissions						
EG (4 tanks)	0.015	12.2	0.2	313		
DEG (1 tank)	Neg	12.2	0.2	313		
TEG (1 tank)	Neg	7.3	0.2	313		
Heavy ends (1 tank)	Neg	7.3	0.2	313		
Handling emissions	0.005					
Fugitive emissions						
Cooling tower	25.192	18.6	5.5	336	220	9.1
Leaks from pumps and valves[c]	0.378					
Secondary emissions from cooling tower blowdown[d]	1.91			305		
			Controlled Emissions			
Process emissions						
Evaporator purge	e					
Evaporator calandria	0.033	12.2	0.08	327	0.002	0.4
Water removal column	Neg	18.3	0.08	327		
EG column	Neg	15.2	0.08	327		
DEG column	Neg	13.7	0.08	327		
TEG column	Neg	13.7	0.08	327		
Fugitive emissions from leaks from pumps and valves[c]	0.130					
Secondary emissions from condensate discharge[d]	4.164			30		

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[a] Total of all vents from source.

[b] Average for each separate vent from source.

[c] Fugitive emissions from leaks are distributed over a 50-m by 150-m area.

[d] Surface of ground-level wastewater treatment system.

[e] Vent from evaporator purge condenser tied to evaporator calandria vent condenser.

APPENDIX C

LIST OF EPA INFORMATION SOURCES

Ableson, P. M., Calcasieu Chemical Corp., letter dated Dec. 20, 1978, in response to EPA's request for information on emissions data on ethylene glycol production facilities.

Dutcher, V.D., Union Carbide Corp., Texas Air Control Board 1975 Emission Inventory Questionnaire for Union Carbide Corp, Seadrift, TX, Plant, Sept. 3, 1976.

Fritsch, J. J., Jr., Celanese Chemical Co., Texas Air Control Board 1975 Emissions Inventory Questionnaire for Celanese Chemical Co., Clear Lake City, TX, plant, May 19, 1976.

Kovacevich, T. R., BASF Wyandotte Corp, letter dated Nov. 27, 1978, in response to EPA's request for information on emissions data on ethylene glycol production facilities.

Lawson, J. F., IT Enviroscience, Inc., Trip Report for Visit to Celanese Chemical Co., Clear Lake City, TX, June 21 and 22, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

Lawson, J. F., IT Enviroscience, Inc., Trip Report for Visit to Union Carbide Corp., South Charleston, WV, Dec. 7, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

Louisiana Air Control Commission, Emission Inventory Questionnaire for Union Carbide Corp., Taft, LA, plant, Mar. 6, 1975.

Louisiana Air Control Commission Permit No. 373 issued Nov. 8, 1974, to Union Carbide Corp., Taft, LA, plant for ethylene oxide/glycol facility, unit 2.

Louisiana Air Control Commission Permit No. 476 issued July 9, 1975, to Union Carbide Corp., Taft, LA, plant for modifications of ethylene oxide/glycol facilities, unit 1.

Mullins, J. A., Shell Oil Co., letter dated Jan. 11, 1979, in response to EPA's request for information on emissions data on ethylene glycol production facilities.

Rogers, P. F., Houston Chemical Co., *Texas Air Control Board 1975 Emissions Inventory Questionnaire* for Houston Chemical Co., Beaumont, TX, plant, May 24, 1976.

Texas Air Control Board Permit No. 1329 issued 1973 to Texas Eastman Co., Longview, TX, for ethylene oxide—ethylene glycol plant.

Texas Air Control Board Permit No. C-3361 issued 1975 to Houston Chemical Co., Beaumont, TX, for ethylene oxide—glycol expansion.

Texas Air Control Board Permit No. 4273 issued 1976 to Dow Chemical USA, Freeport, TX, for ethylene glycol facility.

Texas Air Control Board Permit No. 5032 issued 1977 to Union Carbide Corp., Texas City, TX, for ethylene oxide/ethylene glycol, unit 1.

APPENDIX D

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX E

COST ESTIMATE SAMPLE CALCULATIONS

This appendix contains the sample calculations for the estimated costs presented in this report.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure E-1 illustrates this relationship. A contingency allowance, as indicated on this chart, is included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. E-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +40% to -30%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternate within the limits of accuracy indicated.

In all capital calculations, allowances of 35% were added for magnitude, hazard, and definition contingencies.

This example is based on the use of surface condensers on each process vent in the model plant (see Sect. VI-B-1). The surface condenser for the evaporator calandria vents (A) has 181 sq ft of heat-exchange surface area and requires 40 gpm of cooling water. The surface condensers for the other process vents use the same amount of cooling water as the contact (barometric) condensers in the uncontrolled model plant. The use of surface condensers increases the flow to the waste-water treatment plant by 96 gpm and the BOD by 363 lb/hr. The increase in energy required by treating this additional waste is considered to be negligible.

A. INSTALLED CAPITAL COST

Figure A-1 of the control device evaluation report on condensation[1] shows that the installed capital cost of a carbon steel condenser having 181 sq ft of area is $50,000. The installed capital cost of the other surface condensers is almost the same as for contact condensers for the same service (see Sect. VI-B-1); the difference is considered to be negligible. Therefore the total installed capital cost for the controlled model plant with surface condensers is \$50,000 more than for the uncontrolled model plant with contact condensers on all but one vent.

B. NET ANNUAL COST

From Table VI-2 of this report the total fixed cost, including capital recovery, is 29% of the installed capital cost:

$$\$50{,}000 \times 0.29 = \$14{,}500/\text{yr}.$$

From Table VI-2 the cost of cooling water is \$0.10/1000 gal. The annual cost of 40 gpm of cooling water is

$$\frac{40 \times 60 \times 8760 \times 0.10}{1000} = \$2100/\text{yr}.$$

From Table VI-2 the cost of wastewater treatment is \$0.25/1000 gal plus \$0.10/lb of BOD. To treat the 96 gpm of condensate from all the surface condensers and that contains 363 lb/hr of BOD the annual cost is

$$\frac{96 \times 60 \times 8760 \times 0.25}{1000} = \$12{,}600/\text{yr for flow}$$

$$\text{plus } 363 \times 8760 \times 0.10 = \$318{,}000/\text{yr for BOD}.$$

The total cost of wastewater treatment for the additional condensate is

$$\$12{,}600 + \$318{,}000 = \$330{,}600/\text{yr}.$$

The annual cost summary is as follows:

Fixed	\$ 14,500
Cooling water	2,100
Wastewater treatment	330,600
Total	\$350,000 (rounded)

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[1] D. G. Erikson, IT Enviroscience, Inc., Control Device Evaluation. Condensation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

C. COST EFFECTIVENESS

Cost effectiveness is the net annual cost, \$350,000, divided by the annual VOC reduction. From Table VI-1 the net annual VOC reduction achieved by using surface condensers is

$$9.11 + 794.44 - 71.04 = 733 \text{ Mg/yr (rounded).}$$

The cost effectiveness then is

$$\frac{\$350{,}000}{733} = \$480/\text{Mg of VOC (rounded).}$$

APPENDIX F

EXISTING PLANT CONSIDERATIONS

A. PROCESS CONTROLS

Table F-1 shows the control devices or techniques used by some domestic ethylene glycol producers. For the most part the data available are not current and do not clearly define the emission controls used or the specific vents controlled. Since the data sources (see Appendix C) do not specifically address aqueous wastes nor fugitive and secondary emissions, no data were reported for these categories by most respondents.

The design and operation of the water-removal section of the various existing plants vary extensively and therefore the emissions and emission sources reported also vary. The vapors from the evaporator purge vent are usually condensed. If contact (barometric-type) condensers are used, the condensate ends up in the cooling water. If surface condensers are used, the condensate is usually discharged as wastewater. In some plants heat is recovered by the surface condensers.[1]

The amount of vapor purged from the evaporator may vary, depending on the product end use or product quality requirements. Some plants purge most of the vapor from the first-stage evaporator, as indicated for the model plant. Others may purge a portion of the vapor from the second-stage evaporator. Still other plants may not identify a purge stream as such but instead increase the amount of vapor vented from the evaporator calandria vents.

In newer facilities the ethylene oxide and ethylene glycol plants may be integrated, and common cooling towers, emission controls, and energy-saving techniques be employed. Some plants collect the uncondensed gases from the glycol plant vent condensers and route them back to a flare or thermal oxidizer associated with the ethylene oxide plant.[1,2]

Union Carbide uses an air-cooled condenser on the evaporator calandria vents.[1] Celanese, as well as several other manufacturers, sells the heavy-ends waste product stream to an independent company for recovery of by-products.[3] Some manufacturers may be collecting the condensate from some vents and concentrating the organic for inclusion with the waste product sold. Shell disposes of its wastewater in a disposal well.[4]

Table F-1. Emission Control Devices or Techniques Currently Used by Some Ethylene Glycol Producers*

	Control Devices or Techniques Used				
Producer	Evaporator Purge	Evaporator Calandria	Water Removal Column	Product Distillation Columns	Aqueous Wastes
BASF, Geismar, LA	Not reported	Vent condenser	Barometric condenser	Barometric condenser	Not reported
Calcasieu, Lake Charles, LA	Not reported	None	EO plant flare system	EO plant flare system	Secondary treatment
Celanese, Clear Lake City, TX	Barometric condenser	None	Barometric condenser	Barometric condenser	Not reported
Dow, Freeport, TX	Not reported	None	None	None	Not reported
Eastman, Longview, TX	Not reported	None	None	None	Biological oxidation
PPG, Beaumont, TX	Not reported	None	None	None	Not reported
Shell, Geismar, LA	Barometric condenser	Barometric condenser	Barometric condenser	Barometric condenser	Disposal well
Union Carbide,					
Seadrift, TX	Not reported	None	None	None	Not reported
Taft, LA (Unit 1)	Not reported	None	None	None	Not reported
Taft, LA (Unit 2)	Not reported	Vent condenser	Not reported	None	Not reported
Texas City, TX (proposed)	Not reported	Vent condenser	Not reported	None	Wastewater treatment

*See Appendix C.

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant. The replacement of existing barometric condensers in such a plant with new surface condensers will be significantly more costly than the incremental cost in a new plent where this is merely an alternative.

C. REFERENCES*

1. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Union Carbide Corp., South Charleston, WV, Dec. 7, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).
2. BASF Wyandotte Corp., letter dated Nov. 27, 1978, in response to EPA's request for information on emissions data on ethylene glycol production facilities.
3. Personal communication between R. H. Maurer, Celanese Chemical Co., Inc., Dallas, TX, and R. J. Lovell, IT Enviroscience, Inc., July 23, 1979.
4. Shell Oil Co., letter dated Jan. 11, 1979, in response to EPA's request for information on emissions data on ethylene glycol production facilities.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 9

GLYCOL ETHERS

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CONTENTS OF REPORT 9

Page

I. ABBREVIATIONS AND CONVERSION FACTORS I-1

II. INDUSTRY DESCRIPTION II-1
  A. Introduction II-1
  B. Glycol Ethers Usage and Growth II-1
  C. Domestic Producers II-3
  D. References II-6

III. PROCESS DESCRIPTION III-1
  A. Introduction III-1
  B. Model Process for Manufacture of Ethylene Oxide—Derived Glycol Ethers III-1
  C. Propylene Oxide—Derived Glycol Ethers III-4
  D. Process Variations III-4
  E. References III-5

IV. EMISSIONS IV-1
  A. Model Plant IV-1
  B. Sources and Emissions IV-1
  C. References IV-10

V. APPLICABLE CONTROL DEVICES V-1
  A. Process Sources V-1
  B. Fugitive Sources V-1
  C. Storage and Handling Sources V-1
  D. Secondary Emissions V-1
  E. References V-2

VI. IMPACT ANALYSIS VI-1
  A. Industry Emissions VI-1
  B. References VI-3

APPENDICES OF REPORT 9

Page

A. PHYSICAL PROPERTIES OF GLYCOL ETHER PRODUCTS A-1

B. FUGITIVE-EMISSION FACTORS B-1

TABLES OF REPORT 9

Number		Page
II-1	Usage and Growth of Glycol Ethers	II-2
II-2	Glycol Ethers Capacity	II-4
IV-1	Uncontrolled VOC Emissions——Methanol Process	IV-2
IV-2	Uncontrolled VOC Emissions——Ethanol Process	IV-3
IV-3	Uncontrolled VOC Emissions——Butanol Process	IV-4
IV-4	Model-Plant Storage Tank Data	IV-6
IV-5	Composition of Vacuum System Condensate——Methanol Process	IV-8
VI-1	1978 Industry VOC Emissions	VI-2
A-1	Physical Properties of Ethylene Glycol Monomethyl Ether	A-2
A-2	Physical Properties of Ethylene Glycol Monoethyl Ether	A-2
A-3	Physical Properties of Ethylene Glycol Monobutyl Ether	A-3
A-4	Physical Properties of Diethylene Glycol Monomethyl Ether	A-3
A-5	Physical Properties of Diethylene Glycol Monoethyl Ether	A-4
A-6	Physical Properties of Diethylene Glycol Monobutyl Ether	A-4
A-7	Physical Properties of Triethylene Glycol Monomethyl Ether	A-5
A-8	Physical Properties of Triethylene Glycol Monoethyl Ether	A-5
A-9	Physical Properties of Triethylene Glycol Monobutyl Ether	A-5

FIGURES OF REPORT 9

Number		Page
II-1	Manufacturing Locations of Glycol Ethers	II-5
III-1	Flow Diagram for Uncontrolled Typical Plant	III-2

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

The production of glycol ethers was chosen for study because of its association with the production of ethylene oxide, which, because of projected high volatile organic compound (VOC) emissions, was studied early in the program. Over 90% of the glycol ethers produced are derived from ethylene oxide; the remaining amount is derived from propylene oxide.[1]

This study deals mainly with the production of nine of the ethylene oxide—derived glycol ethers: the methyl, ethyl, and n-butyl monoethers of ethylene glycol, diethylene glycol, and triethylene glycol. In most cases these glycol ethers are produced in the same production facilities.

B. GLYCOL ETHERS USAGE AND GROWTH

The end uses of the ethylene oxide—derived glycol monoethers, the percentage of total production of each, and their expected growth rates are shown in Table II-1. From 1975 to the present almost one-third of the consumption of glycol ethers has been for solvent applications in the protective-coating industry.[1] Due to their chemical structure, the glycol ethers have solvent properties similar to those of alcohols and ethers.[2] Their low evaporation rate makes them well suited as coalescing agents in water-based surface-coating systems, which are beginning to replace solvent-based surface coatings and therefore should be very influential on the growth of glycol ethers. A variety of other uses include solvent applications in hydraulic fluids, printing inks, metal cleaners, and textile dyeing processes and their use as chemical intermediates and jet fuel additives.[1]

The domestic production capacity of the nine major glycol ethers for 1980 is reported to be 555,000 Mg. Applying the projected average annual growth rate of 5%/yr during the years 1977—1982 to the 1977 production figure of 297,000 Mg indicates that ~62% of this production capacity will be utilized in 1980. No shortage of ethylene oxide is expected during this period.[3]

The glycol ethers derived from propylene oxide are used as coupling agents in hydraulic fluids and as solvents by the coating industry for water-based paints. The 1977 production was reported to be 20,000 Mg, with a projected annual growth

514

Table II-1. Usage and Growth of Glycol Ethers*

Compound	End Use	1977 Production Split (%)	Projected Average Annual Growth (1977-1982) (%)
Ethylene glycol			
Monomethyl ether	Jet fuel additive; solvent in protective coatings; additive to textile and leather dyeing processes	17	5.2
Monoethyl ether	Production of ethylene glycol monoethyl ether acetate; solvent for protective coatings and printing inks	36	4.0
Monobutyl ether	Solvent for protective coatings; diluent in hydraulic brake fluids, rust removers, insecticides, and herbicides	26	6.7
Diethylene glycol			
Monomethyl ether	Solvent in wood stains, lacquers, stamp pad inks, diluent for hydraulic brake fluids, coalescing agent for latex paints	3	5
Monoethyl ether	Diluent for hydraulic brake fluids, solvent for protective coatings, textile printing and dyeing	5	5
Monobutyl ether	Production of diethylene glycol monobutyl ether acetate, coalescing agent in latex paints, solvent for stamp pad inks, dyes, diluent for hydraulic brake fluids	5	5.5
Triethylene glycol			
Monomethyl ether	Diluent in brake fluids, solvent in protective coatings	4	5.7
Monoethyl ether		3	
Monobutyl ether		1	

*From ref 1.

rate of consumption of 6—6.5% through 1982. On this basis the projected 1982 consumption of glycol ethers from propylene oxide will be approximately 27,000 Mg.[1]

C. DOMESTIC PRODUCERS

According to 1980 figures there are seven domestic companies producing ethylene oxide—derived glycol ethers at ten plants. Table II-2 lists the producers and their rated capacities.[1] Figure II-1 shows the plant locations.

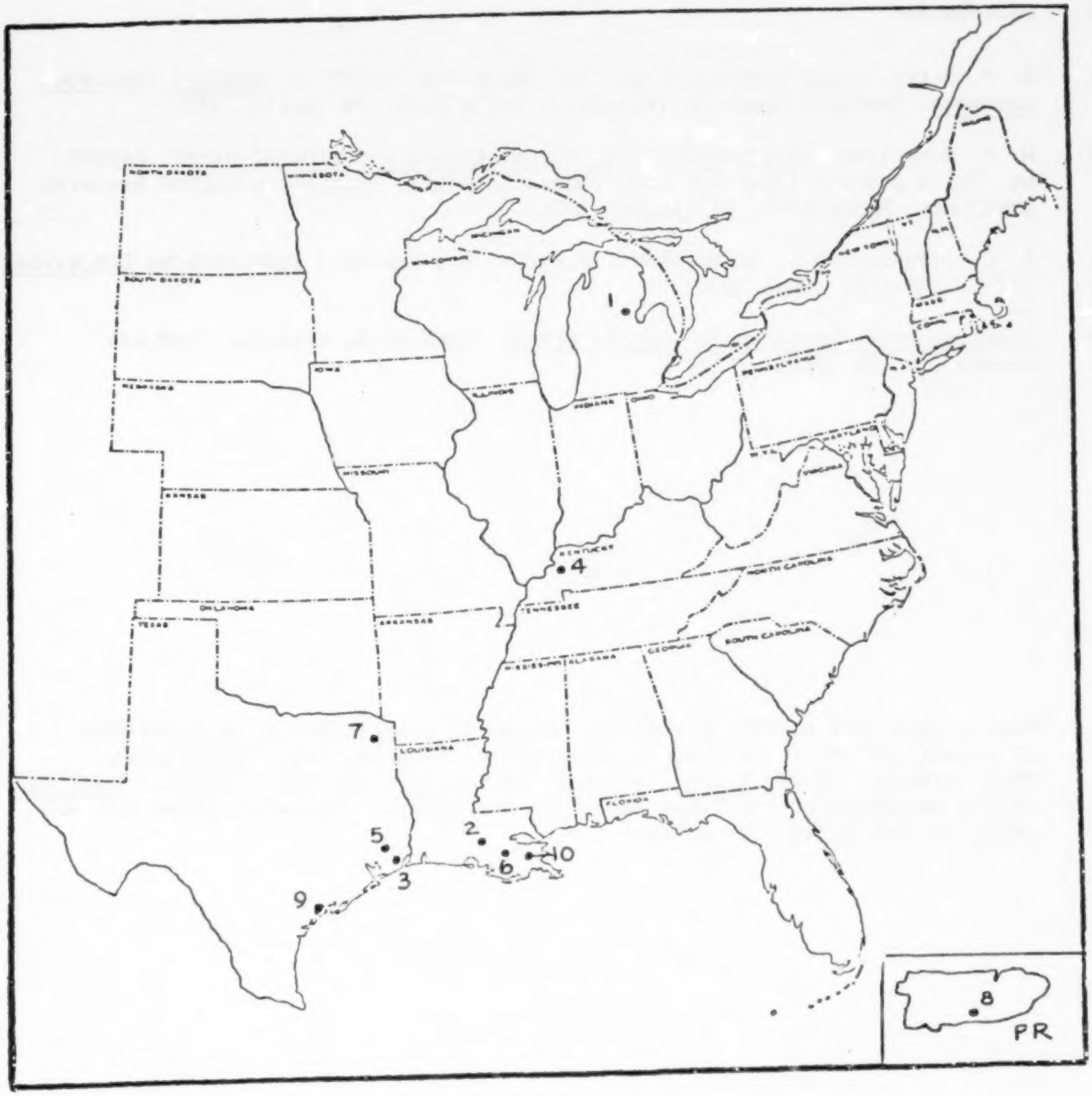
The three companies that produce propylene oxide—derived glycol ethers are the Dow Chemical Company, Olin Corporation, and Union Carbide Corporation.

Table II-2. Glycol Ethers Capacity[a]

	1980 Capacity (10^3 Mg)[b]
Dow, Midland, MI	95
Dow, Plaquemine, LA	54
Jefferson, Port Neches, TX	18
Olin, Brandenberg, KY	32
PPG Industries, Beaumont, TX	9
Shell, Geismar, LA	25
Texas Eastman, Longview, TX	100
Union Carbide Ponce, PR Seadrift, TX Taft, LA	222
Total	555

[a] From ref 1.

[b] Capacity amounts are flexible since they depend on the product mix. Some capacities also include the capability for producing propylene oxide—derived glycol ethers.



1. Dow, Midland, MI
2. Dow, Plaquemine, LA
3. Jefferson, Port Neches, TX
4. Olin, Brandenberg, KY
5. PPG Industries, Beaumont, TX
6. Shell, Geismar, LA
7. Texas Eastman, Longview, TX
8. Union Carbide, Ponce, PR
9. Union Carbide, Seadrift, TX
10. Union Carbide, Taft, LA

Fig. II-1. Manufacturing Locations of Glycol Ethers

D. REFERENCES*

1. R. T. Gerry, "Glycol Ethers," pp. 663.5021B—663.5022Y in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1979).

2. H. W. Scheeline, Ethylene Glycols, Glycol Ethers and Ethanolamines, Report No. 70, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (August 1971).

3. S. C. Johnson, "U.S. EO/EG—Past, Present, and Future," Hydrocarbons Processing 55(6), 109—113 (June 1976).

4. Chemical Products Synopsis, Glycol Ethers, Mannsville Chemical Products, Mannsville, NY (April 1978).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

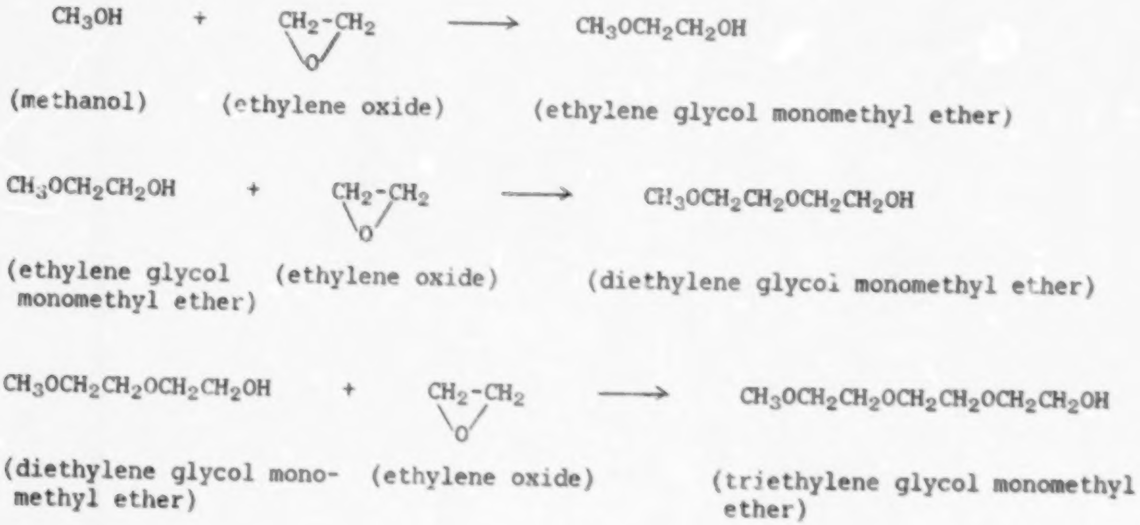
III. PROCESS DESCRIPTIONS

A. INTRODUCTION

The reaction of ethylene oxide with anhydrous methyl, ethyl, or n-butyl alcohol is the only process that is commercially practiced in the United States for the production of ethylene oxide—based glycol ethers.[1] Similarly, glycol ethers derived from propylene oxide are formed from the reaction of alcohols with propylene oxide.

B. MODEL PROCESS FOR MANUFACTURE OF ETHYLENE OXIDE—DERIVED GLYCOL ETHERS

The ethylene glycol monoethers are produced by the following sodium hydroxide catalyzed chemical reactions.[2] Only the reactions with methanol are shown; however, the primary alcohols, ethanol and butanol, react similarly to produce the ethyl and butyl ethers.


CH3OH
+
CH2-CH2
O
CH3OCH2CH2OH
(methanol)
(ethylene oxide)
(ethylene glycol monomethyl ether)
CH3OCH2CH2OH
+
CH2-CH2
O
CH3OCH2CH2OCH2CH2OH
(ethylene glycol monomethyl ether)
(ethylene oxide)
(diethylene glycol monomethyl ether)
CH3OCH2CH2OCH2CH2OH
+
CH2-CH2
O
CH3OCH2CH2OCH2CH2OCH2CH2OH
(diethylene glycol monomethyl ether)
(ethylene oxide)
(triethylene glycol monomethyl ether)

The mono-, di-, and triethylene glycol products are produced simultaneously. The reaction and recovery operations are continuous.

The model continuous process for the manufacture of the glycol ethers is shown in Fig. III-1. The sodium hydroxide catalyst (stream 1) (acid catalyst can be used) and one of the anhydrous primary alcohols——methanol, ethanol, or n-butanol (stream 2)——are blended in the mix tank.[3] The material from the alcohol catalyst storage tank is combined with ethylene oxide (stream 3) and with the recycled

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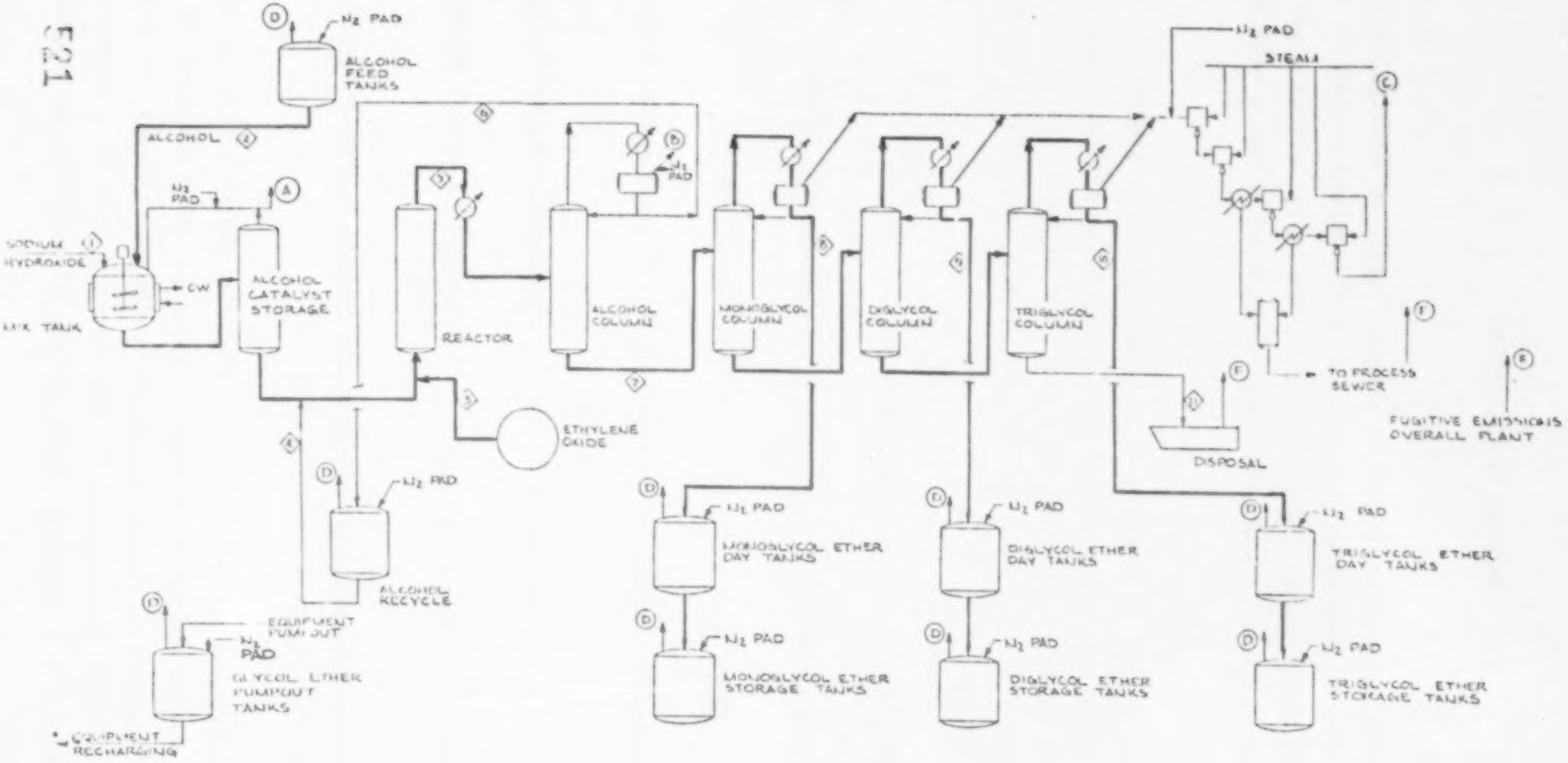


Fig. III-1. Flow Diagram for Uncontrolled Model Plant Producing Glycol Ethers from Ethylene Oxide

alcohol (stream 4) and is then fed to the reactor. The reaction is carried out at an elevated pressure (2.5×10^6 to 4.6×10^6 Pa) and temperature (200 to 230°C). The reaction between ethylene oxide and the alcohols is exothermic (20 to 25 kg-cal per g-mole of ethylene oxide reacted).[4]

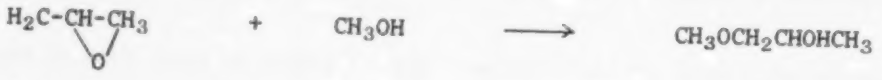
Ethylene oxide reacts with some of the ethylene glycol ether to form diethylene glycol ether and with some of the diethylene glycol ether to form triethylene glycol ether. The reaction product consists of a mixture of mono-, di-, and triethylene glycol ethers, as well as some higher molecular weight glycol ethers.[2] The reaction mixture product distribution is influenced by the alcohol:ethylene oxide ratio in the reaction feed. A higher alcohol:ethylene oxide ratio reduces the formation of higher glycol ethers.

The product stream (5) exits the reactor and is sent to the alcohol distillation column, where excess alcohol is distilled overhead and recycled (stream 6) for future reaction. The column is normally operated at atmospheric pressure although, for the higher alcohols, it could be operated under a slight vacuum. The alcohol column bottoms (stream 7) are then sent to the monoethylene glycol ether column, where monoethylene glycol ether is vacuum distilled and sent (stream 8) to product storage via one of the two monoglycol ether day tanks. Similarly, diethylene glycol ether and triethylene glycol ether are vacuum distilled consecutively in two more distillation columns. The vacuum system normally consists of a four-stage steam-jet series with surface intercondensers. The diethylene glycol ether product (stream 9) and triethylene glycol ether product (stream 10) streams are sent to their respective storage tanks.[2] The heavy ends (stream 11) from the triethylene glycol ether column is disposed of.[3] No data were available on the disposal of this stream; however, it is probably incinerated or landfilled.

When product lines are switched, the process equipment is drained to one of the three pump-out tanks. The contents of the pump-out tank containing the next product line to be produced is then charged to the process. The columns are put on total reflux, feed is slowly started, and the product streams are returned to the pump-out tank until product specification is attained. When specifications are met, the feed is increased to design levels and the product streams are sent to the day tanks.

C. PROPYLENE OXIDE—DERIVED GLYCOL ETHERS

The propylene glycol monoethers are produced by the following reaction. The most important family of these ethers utilize methanol as the primary alcohol.[5]



$$H_2C\text{-}CH\text{-}CH_3 \text{ (epoxide, O)} + CH_3OH \longrightarrow CH_3OCH_2CHOHCH_3$$

(propylene oxide) (methanol) (propylene glycol monomethyl ether)

As in the ethylene oxide—derived process, the propylene glycol monomethyl ethers formed in the reactor react further with the propylene oxide to form di- and tripropylene glycol monomethyl ethers. An excess of anhydrous methanol limits the formation of these higher ethers. In some cases the same equipment is believed to be used for the production of ethylene oxide.

D. PROCESS VARIATIONS

Jefferson Chemical Company produces only methyl and ethyl glycol ethers from ethylene oxide. Their production unit has only two distillation towers; therefore the unit must be operated in two separate passes to recover both mono- and di-ethers.[6]

E. REFERENCES*

1. J. L. Blackford, "Glycol Ethers," pp. 663.5021B—663.5022Y in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (November 1976).

2. H. W. Scheeline, Ethylene Glycols, Glycol Ethers and Ethanolamines, Report No. 70, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (August 1971).

3. T. L. Schomer, IT Enviroscience, Inc., Trip Report to Dow Chemical Co., Midland, MI Feb. 10, 1978 (on file at EPA, ESED Research Triangle Park, NC).

4. R. N. Shreve and L. F. Albright, "Alkylation," Chap. 14, p. 804, in McGraw-Hill Series in Chemical Engineering, "Unit Processes in Organic Synthesis," P. H. Groggins, editor-in-chief, McGraw-Hill Book Co., New York, 1958.

5. J. L. Blackford, "Propylene Oxide," pp. 690.8021B—690.8022C in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (November 1976).

6. J. F. Cooper, Jefferson Chemical Company, letter dated July 11, 1979, to David R. Patrick, EPA, Research Triangle Park, NC.

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IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. MODEL PLANT

The glycol ether capacity selected for the model plant is 45,400 Mg/yr. For this study the nine major glycol ethers that utilize methanol, ethanol, and n-butanol as raw materials are produced in the same process equipment on a part-time basis. The relative amounts of each glycol ether produced in the United States in 1975 formed the basis for the following production capacity split for the model plant: 10,800 Mg of methyl glycol ethers, 19,000 Mg of ethyl glycol ethers, and 15,600 Mg of n-butyl glycol ethers.*

The model plant is assumed to operate 8256 hr a year, with 504 hr a year allotted for process down time required for switching from one alcohol-based glycol ether product line to another. This is common practice in most of the industry. However, some production facilities utilize only one of the alcohols mentioned,[1] in which case the plant would not require time for switching product lines and would not require as many storage tanks. In either case the process equipment requirements would be the same.

B. SOURCES AND EMISSIONS

Emission sources and uncontrolled emission rates of VOC for the model plant producing methanol-, ethanol-, and n-butanol-based glycol ethers are summarized in Tables IV-1, IV-2, and IV-3 and are discussed below.

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*In order to minimize the revision time, the 1975 production split that was used for the original draft of this report is used rather than the 1977 split. For our purposes the differences are not believed to be significant.

Table IV-1. Uncontrolled Emissions of Total VOC from the Production of Methanol-Based Glycol Ethers[a]

Source	Stream Designation (Fig.III-1)	Total VOC Emissions Ratio[b] (g/kg)	Total VOC Emissions Rate (kg/hr)
Catalyst-methanol mix tank[c]	A	0.0097	0.05
Methanol recovery column vent[d]	B	0.15	0.82
Vacuum system vent[c]	C	0.013	0.07
Storage vents	D	0.24	0.30[e]
Fugitive emissions	E	0.19	1.04
Secondary emissions	F	0.03	0.14

[a] Emission ratios and emission rates apply only to methyl glycol ether production, which is 1960 hr/yr; the annual production is 1.08 X 10^7 kg for model plant.

[b] g of emission per kg of methyl glycol ethers produced.

[c] See ref 2.

[d] See ref 2 for inert-gas flow from alcohol column.

[e] Weighted average of storage emissions for 8760 hr/yr.

Table IV-2. Uncontrolled Emissions of Total VOC from the Production of Ethanol-Based Glycol Ethers[a]

Source	Stream Designation (Fig.III-1)	Total VOC Emissions	
		Ratio[b] (g/kg)	Rate (kg/hr)
Catalyst-ethanol mix tank[c]	A	0.006	0.03
Ethanol recovery column vent[d]	B	0.093	0.51
Vacuum system vent[e]	C	0.013	0.07
Storage vents	D	0.17	0.37[f]
Fugitive emissions	E	0.19	1.04
Secondary emissions	F	0.03	0.14

[a] Emission ratios and emission rates apply only to ethyl glycol ether production, which is 3450 hr/yr; the annual production is 1.90 X 10^7 kg for model plant.

[b] g of emission per kg of ethyl glycol ethers produced.

[c] Calculated from catalyst-methanol mix tank emission (Table IV-1) number and ratios of vapor pressure and molecular weight of ethanol to methanol.

[d] See ref 2 for inert-gas flow from alcohol column.

[e] See ref 2.

[f] Weighted average of storage emissions for 8760 hr/yr.

Table IV-3. Uncontrolled Emissions of Total VOC from the Production of Butanol-Based Glycol Ethers[a]

Source	Stream Designation (Fig.III-1)	Total VOC Emissions Ratio[b] (g/kg)	Total VOC Emissions Rate (kg/hr)
Catalyst-butanol mix tank[c]	A	0.001	0.005
Butanol recovery column vent[d]	B	0.016	0.09
Vacuum system vent[e]	C	0.013	0.07
Storage vents	D	0.10	0.17[f]
Fugitive emissions	E	0.19	1.04
Secondary emissions	F	0.03	0.14

[a] Emission ratios and emission rates apply only to butyl glycol ether production. Butyl glycol ether production is 2850 hr/yr; the annual production is 1.56×10^7 kg for model plant.

[b] g of emission per kg of butyl glycol ethers produced.

[c] calculated from catalyst-methanol mix tank emission (Table IV-1) and ratios of vapor pressure and molecular weight of butanol to methanol.

[d] See ref 2 for inert-gas flow from alcohol column.

[e] See ref 2.

[f] Weighted average of storage emissions for 8760 hr/yr.

1. Alcohol-Catalyst Mix Tank and Storage Tank Vents

The mix tank and storage tank are blanketed with nitrogen to maintain anhydrous conditions (vent A, Fig. III-1); otherwise the water present will contaminate the glycol ethers. This vent stream contains nitrogen and, depending on the product line being made, one of the three alcohols—methanol, ethanol, or *n*-butanol. The emission data shown in Table IV-1 for the mix-tank vent for methyl ethers were provided by industry.[2] The emissions from this vent for ethyl and *n*-butyl ethers, shown in Tables IV-2 and IV-3 respectively, were calculated from the methyl ethers emission and the ratios of molecular weight and vapor pressure of ethanol and butanol to methanol. Much of the heat generated from the dissolution of sodium hydroxide in alcohol is removed in the mix tank with cooling water; therefore no appreciable fluctuation occurs in the temperature of the vessel contents or in the alcohol emissions.

2. Alcohol Recovery Column Vent

This vent emits alcohol and inert gases from the alcohol column reflux tank (source B). The purpose of the inert-gas stream is to prevent moisture in the air from contacting the alcohol. The total uncontrolled VOC emission rates from this vent during capacity production of the methanol-, ethanol-, and n-butanol-based glycol ethers are 0.82 kg/hr, 0.51 kg/hr, and 0.09 kg/hr respectively.

3. Vacuum System Vent[2]

The vent (C, Fig. III-1) from the vacuum system contains water vapor, inert gases, and a small percentage of VOC. The total uncontrolled VOC emission rate is estimated to be 0.07 kg/hr for the model plant operating at capacity. This rate was estimated by an industrial producer of methyl glycol ethers. Since this emission is small and emission data were not available for this stream during production of ethyl and butyl glycol ethers, the emission is assumed to be the same for all three product lines.

4. Storage and Handling Emissions

Emissions result from the storage and handling of the glycol ether products and the alcohol raw materials. Sources (D) of the losses are shown in Fig. III-1. All storage tanks are blanketed with nitrogen to maintain anhydrous conditions. Storage tank parameters for the model plant are given in Table IV-4. Since

Table IV-4. Model-Plant Storage Tank Data

Storage Facility	Contents	No. of Tanks Required	Tank Size (m^3)	Turnovers per Year	Bulk Temperature (°C)
Feed tanks	Methanol	1	757	6	20
	Ethanol	1	1136	10	20
	Butanol	1	1893	6	20
	Ethylene oxide	1	1325	21	10
Recycle tanks	Methanol	1	15	5	20
	Ethanol	1	23	5	20
	Butanol	1	11	5	20
Product day tanks	Ethylene glycol ethers	2	114	164[a]	60
	Diethylene glycol ethers	2	17	169[b]	60
	Triethylene glycol ethers	2	26	97[c]	60
Product storage tanks	Ethylene glycol methyl ether	1	1135	6	20
	Ethylene glycol ethyl ether	1	1702	9	20
	Ethylene glycol butyl ether	1	2270	6	20
	Diethylene glycol methyl ether	1	170	6	20
	Diethylene glycol ethyl ether	1	265	9	20
	Diethylene glycol butyl ether	1	378	6	20
	Triethylene glycol methyl ether	1	416	6	20
	Triethylene glycol ethyl ether	1	189	9	20
	Triethylene glycol butyl ether	1	151	6	20
Product pump-out tanks	Methanol, mono-, di-, and triethylene glycol methyl ethers	1	8	1	20
	Ethanol, mono-, di-, and triethylene glycol ethyl ethers	1	8	1	20
	Butanol, mono-, di-, and triethylene glycol butyl ethers	1	8	1	20

[a] 32 turnovers for production of methyl ethers, 70 for ethyl ethers, and 62 for butyl ethers.

[b] 30 turnovers for production of methyl ethers, 72 for ethyl ethers, and 67 for butyl ethers.

[c] 49 turnovers for production of methyl ethers, 32 for ethyl ethers, and 16 for butyl ethers.

ethylene oxide is stored in a pressurized tank, none of it is emitted. The uncontrolled storage and handling emission rates in Tables IV-1, IV-2, and IV-3 are based on fixed-roof tanks, half full, and a diurnal temperature variation of 22°C and the use of the emission equations from AP-42.[3] However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overpredicts emissions.

The losses from the multiuse day tanks are assigned to a product line only during the period that product is being produced, while the losses from the feed, recycle, product storage, and product pump-out tanks are assigned to the product line for which they are used. It is assumed that all feed and product storage tanks are left half full when the product line they are assigned to is not being produced; therefore breathing losses from these tanks occur all year. The storage losses from each product line expressed as emission rates in Tables IV-1, IV-2, and IV-3 are prorated for the entire year.

5. Fugitive Emissions

Process pumps and valves are potential sources of fugitive emissions. The typical plant is assumed to have 34 pumps, 300 process valves, and 30 pressure relief valves handling VOC. The fugitive emission factors from Appendix B were applied to the valve and pump count to determine the uncontrolled fugitive emission rate of 4.4 kg/hr from the model plant. It is assumed that the fugitive emissions rate remains constant throughout the year, regardless of the product line being produced.

6. Secondary Emissions

Secondary VOC emissions can result from the handling and disposal of process-waste streams. Two potential sources (F) are indicated in Fig. III-1 for the model plant. The composition of the aqueous condensate stream from the vacuum system during methanol-based glycol ether production is shown in Table IV-5. Data are not available on the composition of this stream during ethanol- and butanol-based glycol ether production; however, the hydrocarbon composition is expected to be approximately the same during production of all three alcohol-based glycol ethers. The emission rate from this source is estimated to be 0.01 kg/hr, assuming that the emissions are the same for all product lines.

Table IV-5. Composition of Aqueous Condensate Stream from Vacuum System During Methanol-Based Glycol Ether Production[a]

Stream Composition	Production Ratio[b] (g/kg)
Water	350
Methanol	∿0.063
Ethylene glycol methyl ether	∿0.094
Diethylene glycol methyl ether	∿0.063
Triethylene glycol ethyl ether	∿0.015
Total hydrocarbons	∿0.235

[a] From ref 2.

[b] g of component per kg of glycol ether produced.

Disposal of the bottoms from the triethylene glycol column represents another potential secondary emission. The uncontrolled secondary emission of total VOC from this source for the model plant operating at capacity has been estimated from data supplied by industry to be 0.13 kg/hr.[4]

7. Process Variation

One manufacturer indicated that the overheads from the alcohol column are subcooled to 25 to 30°C by the column condenser.[2] This subcooling reduces the vapor pressure of the condensed overheads and therefore reduces the amount of VOC emissions through the alcohol vent. This procedure is known to be practiced in the glycol ether industry but not necessarily by all manufacturers.

C. REFERENCES*

1. H. W. Scheeline, Ethylene Glycol, Glycol Ethers and Ethanolamines, Report No. 70, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (August 1971).

2. T. L. Schomer, IT Enviroscience, Inc., Trip Report to Union Carbide Corp., South Charleston, WV, Feb. 13, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. C. C. Masser, "Storage of Petroleum Liquids," p. 4.3-6 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed., U.S. EPA, Research Triangle Park, NC (August 1977)

4. T. L. Schomer, IT Enviroscience, Inc., Trip Report to Dow Chemical Co., Midland, MI, Feb. 10, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

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V. APPLICABLE CONTROL DEVICES

A. PROCESS SOURCES

Process emissions from the model plant occur from vents A, B, and C. (See Fig. III-1 for vent locations and Tables IV-1, IV-2, and IV-3 for uncontrolled emissions.)

The sum of the process emission rates for the glycol ether processes based on methanol, ethanol, and butanol are 0.94 kg of VOC/hr, 0.61 kg of VOC/hr, and 0.16 kg of VOC/hr respectively. Since there is a relatively small quantity of process VOC emissions, due primarily to the low volatility of the products, no emission control devices have been identified.[1,2]

B. FUGITIVE SOURCES

Controls for fugitive sources will be discussed in a future document covering fugitive emissions from the synthetic organic chemicals manufacturing industry (SOCMI).

C. STORAGE AND HANDLING SOURCES

Controls for SOCMI storage emissions are discussed in a separate EPA document.[3]

D. SECONDARY EMISSIONS

Secondary emissions for SOCMI are covered by a separate EPA document.[4]

E. REFERENCES*

1. T. L. Schomer, IT Enviroscience, Inc., Trip Report to Union Carbide Corp., South Charleston, WV, Feb. 13, 1978 (data on file at EPA, ESED, Research Triangle Park, NC).

2. T. L. Schomer, IT Enviroscience, Inc., Trip Report to Dow Chemical Co., Midland, MI, Feb. 10, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. D. G. Erikson, IT Enviroscience, Inc., Emission Control Options for the Synthetic Organic Chemicals Manufacturing Industry——Storage and Handling Report (EPA, ESED, Research Triangle Park, NC) (October 1978).

4. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions Report (EPA, ESED, Research Triangle Park, NC) (October 1979).

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VI. IMPACT ANALYSIS

A. INDUSTRY EMISSIONS

The information available from industry indicates that no emission control devices are utilized in glycol ether production facilities to control process emissions.[1,2] Tables IV-1, IV-2, and IV-3 show that the process emissions from the methyl, ethyl, and n-butyl glycol ether processes are small.

The production of glycol ethers from ethylene oxide in 1978 is estimated at 281,000 Mg.[3] The emissions associated with this production are shown in Table IV-1. Emission factors from Sect. IV were used to calculate the emissions in Table VI-1. The production split of methyl, ethyl, and n-butyl glycol ethers is assumed to be the same as the split reported in Sect. IV-A for 1975.

Fugitive emissions were calculated by using the fugitive emissions factors of Appendix B and are estimated to comprise over one-third of the total emissions from the glycol ethers manufacturing industry.

Table VI-1. 1978 Industry VOC Emissions from Glycol Ether Production Using Ethylene Oxide

	VOC Emissions (Mg/yr)			
Source	Methyl Glycol Ethers	Ethyl Glycol Ethers	Butyl Glycol Ethers	Total Glycol Ethers
Process emissions[b]	11.6	13.1	2.9	27.6
Storage vents[b]	35.5	41.0	20.4	96.9
Fugitive emissions[c]	18.6	32.9	27.2	78.7
Secondary emissions[d]	2.0	3.5	2.9	8.4
				211.6

[a] 1978 glycol ether production, 281,000 Mg total (67,000 Mg of methyl glycol ethers; 117,000 Mg of ethyl glycol ethers; and 97,000 Mg of butyl glycol ethers).

[b] Calculated from Tables IV-1 through Table IV-3.

[c] Controlled fugitive emission factor is 0.28 g/kg.

[d] Secondary emission ratio from Tables IV-1 through IV-3.

B. REFERENCES

1. T. L. Schomer, IT Enviroscience, Inc., Trip Report to Union Carbide Corp., South Charleston, WV, Feb. 13, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. T. L. Schomer, IT Enviroscience, Inc., Trip Report to Dow Chemical Co., Midland, MI, Feb. 10, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. 1978 Directory of Chemical Producers, United States of America, Chemical Information Services, p. 645, Stanford Research Institute, Menlo Park, CA.

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Appendix A

PHYSICAL PROPERTIES OF GLYCOL ETHER PRODUCTS

The data sources for the physical properties given in the following tables are as follows.

Table A-1: J. Dorigan *et al*., "Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals D-E)," MTR-7248, Rev. No. 1, Appendix II, p. AII-292, Mitre Corp. (September 1976).

Table A-2: MTR-7248, App. II, p. AII-286; also: *Welcome to the World of Dow Products and Services*, Catalog of Dow Products, pp. 6 and 7, 1971.

Table A-3: MTR-7248, App. II, p. AII-284; Dow Catalog, p. 6.

Table A-4: MTR-7248, App. II, p. AII-98; Dow Catalog, p. 6.

Table A-5: MTR-7248, App. II, p. AII-92; Dow Catalog, p. 6.

Table A-6: MTR-7248, App. II, p. A-88; Dow Catalog, p. 6.

Table A-7: J. Dorigan *et al*., "Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals O-Z)," MTR-7248, Rev. No. 1, Appendix IV, p. AIV-268, Mitre Corp. (September 1976).

Table A-8: G. G. Hawley, *The Condensed Chemical Dictionary*, 8th Ed., p. 356, Van Nostrand Reinhold, New York, 1971.

Table A-9: *Ibid*., p. 136.

Table A-1. Physical Properties of Ethylene Glycol Monomethyl Ether

Synonyms	2-Methoxyethanol, ethoxyacetate
Molecular formula	$C_3H_8O_2$
Molecular weight	76.1
Vapor pressure	6.2 mm Hg at 20°C
Melting point	-81.5°C
Boiling point	124.5°C at 1 atm
Density	0.966 g/ml at 20°C/4°C
Physical state	Liquid
Water solubility	Infinite

Table A-2. Physical Properties of Ethylene Glycol Monoethyl Ether

Synonyms	2-Ethoxyethanol
Molecular formula	$C_4H_{10}O_2$
Molecular weight	90.1
Vapor pressure	3.8 mm Hg at 20°C
Pour point	-100°C
Boiling point	135.1°C
Density	0.9360 g/ml at 50°C/15°C
Physical state	Liquid
Water solubility	Infinite

Table A-3. Physical Properties of Ethylene Glycol Monobutyl Ether

Synonyms	2-Butoxyethanol
Molecular formula	$C_6H_{14}O_2$
Molecular weight	118.2
Vapor pressure	0.76 mm Hg at 20°C
Pour point	-75°C
Boiling point	171.2°C
Density	0.9027 g/ml at 20°C/4°C
Physical state	Liquid
Water solubility	Infinite

Table A-4. Physical Properties of Diethylene Glycol Monomethyl Ether

Synonyms	2-(2-Methoxyethoxy)ethanol
Molecular formula	$C_5H_{12}O_3$
Molecular weight	120.2
Vapor pressure	0.2 mm Hg at 20°C
Pour point	-85°C
Boiling point	194.2°C
Density	1.0354 g/ml at 20°C/4°C
Physical state	Liquid
Water solubility	Infinite

Table A-5. Physical Properties of Diethylene Glycol Monoethyl Ether

Synonyms	2-(2-Ethoxyethoxy)ethanol
Molecular formula	$C_6H_{14}O_3$
Molecular weight	134.2
Vapor pressure	<1.0 mm Hg at 20°C
Pour point	-90°C
Boiling point	201.9°C
Density	0.9902 g/ml at 20°C/4°C
Physical state	Liquid
Water solubility	Infinite

Table A-6. Physical Properties of Diethylene Glycol Monobutyl Ether

Synonyms	2-(2-Isobutoxyethoxy)ethanol
Molecular formula	$C_8H_{18}O_3$
Molecular weight	162.2
Vapor pressure	0.01 mm Hg at 20°C
Pour point	-68.1°C
Boiling point	230.6°C
Density	0.9536 g/ml at 20°C/20°C
Water solubility	Infinite

Table A-7. Physical Properties of Triethylene Glycol Monomethyl Ether

Synonyms	2-[2-(2-Methoxyethoxy)ethoxy] ethanol, methoxytriglycol, methoxytriethylene glycol
Molecular formula	$C_7H_{16}O_4$
Molecular weight	164.2
Vapor pressure	<0.01 mm Hg at 20°C
Boiling point	249°C
Density	1.0494 g/ml
Physical state	Liquid
Water solubility	Infinite

Table A-8. Physical Properties of Triethylene Glycol Monoethyl Ether

Synonyms	Ethoxytriglycol
Molecular formula	$C_2H_5O(C_2H_4O)_3H$
Molecular weight	178
Vapor pressure	<0.01 Hg at 20°C
Melting point	-18.7°C
Boiling point	255.4°C
Density	1.021 g/ml at 20°C/20°C
Physical state	Liquid
Water solubility	Infinite

Table A-9. Physical Properties of Triethylene Glycol Monobutyl Ether

Synonyms	Butoxytriglycol
Molecular formula	$C_4H_9O(C_2H_4O)_3H$
Molecular weight	206.3
Vapor pressure	<0.01 mm Hg at 20°C/20°C
Physical state	Liquid
Water solubility	Infinite

APPENDIX B

FUGITIVE EMISSION FACTORS

Fugitive emission factors established for petroleum refinery operation and published in AP-42 are based on emission quantities per unit throughput and therefore are unsatisfactory for use here.[1] The emission factors for each equipment component used in this report are based on the orginal emission studies[2--4] used to establish the AP-42 factors with assumptions as follows:

1. Pump Seals (including standby pumps)
    a. "Uncontrolled" is the average loss measured for mechanical seals.
    b. "Controlled" is the average loss for mechanical seals, with major leaks assumed to be fixed.

	Uncontrolled	Controlled
Pump seals (kg/day/seal)	1.5	0.16

2. Compressor Seals
    a. "Uncontrolled" is the average loss measured for all seals venting to atmosphere.
    b. "Controlled" is the average loss based on the large leaks being fixed.

	Uncontrolled	Controlled
Compressor seals (kg/day/seal)	3.9	1.0

3. Valves
    a. "Uncontrolled" is the average loss measured for all valves.
    b. "Controlled" is the average loss, with the large leaks assumed to be fixed.

	Uncontrolled	Controlled
Pipeline valves (kg/day/valve)	0.068	0.006

4. Pressure Relief Devices
   a. "Uncontrolled" is the average loss measured for all valves.
   b. "Controlled" is the average loss based on the assumption that the large leaks are fixed.

	Uncontrolled	Controlled
Pressure relief devices (kg/day/valve)	1.1	0.1

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[1] W. M. Vatavak, "Petroleum Industry," pp. 9.1-1 to 9.1-8 in Compilation of Air Pollutant Emission Factors, 2d ed., AP-42, EPA, Research Triangle Park, NC (March 1975).

[2] R. K. Palmer, Hydrocarbon Losses from Valves and Flanges. Report No. 2, PB-216-682, Joint District, Federal and State Project for the Evaluation of Refinery Emissions. Air Pollution Control District, County of Los Angeles, CA (March 1957).

[3] B. J. Steigerwald, Emissions of Hydrocarbons to the Atmosphere from Seals on Pumps and Compressors. Report No. 6, PR-216-582, Joint District, Federal and State Project for the Evaluation of Refinery Emissions. Air Pollution Control District, County of Los Angeles, CA (April 1958).

[4] B. J. Steigerwald, Hydrocarbon Leakage from Pressure Relief Valves. Report No. 3, PB-216-715, Joint District, Federal and State Project for the Evaluation of Refinery Emissions. Air Pollution Control District, County of Los Angeles, CA (May 1957).

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